STUDIES IN CHEMISTRY

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CONTENTS

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ABSTRACT

Studies have been carried out in the following areas:

(1) Photochemistry

The photochemical behaviour of selected aromatic carbonyl compounds has been studied, especially in relation to the nature of the excited state involved in chemical reaction. The photochemistry of certain pyrimidine-based agrochemicals and related compounds has been investigated from a kinetic and product viewpoint. The dye sensitised photooxidation of these compounds has also been studied.

(2) Spectroscopy and Charge-Transfer Complexation

The spectroscopic properties and electron acceptor ability of a variety of organic compounds has been reported upon.

(3) Chemistry of Polynitroaromatic Compounds

The synthesis of a number of new polynitronaphthalenes and polynitroacenaphthenes has been achieved, and the properties of many of these compounds has been studied by nmr, esr, electronic spectroscopy and by mass spectrometry. The reaction of base with such compounds has also been investigated.

(4) Education

Articles have been published in educational journals on molecular complexes, colour, solar energy and spectroscopy. Textbooks on molecular spectroscopy and photochemistry have been published.

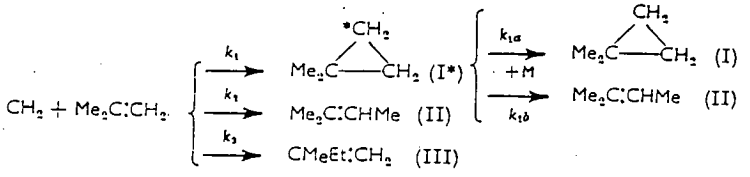
LIST OF PUBLICATIONS

Preprinted from the Journal of the Chemical Society,
August, 1958, (588), pages 2897—2898.

588. *Reactions of Methylene with* iso*Butene.*

By J. H. Knox, A. F. Trotman-Dickenson, and C. H. J. Wells.

The reactions of methylene with *iso*butene have been studied by photolysing keten in the presence of the olefin (ratio 1 : 2·8) in a Pyrex vessel with light from a medium-pressure mercury arc. The products were analysed by gas chromatography and identified by their infrared spectra. The formation of products may be interpreted in terms of the following scheme:



The variation of the yields of (I), (II), and (III) with pressure, shown in Fig. 1 for 20°, indicate that at pressures above about 4 cm. effectively all the (I*) molecules are

Fig. 1.

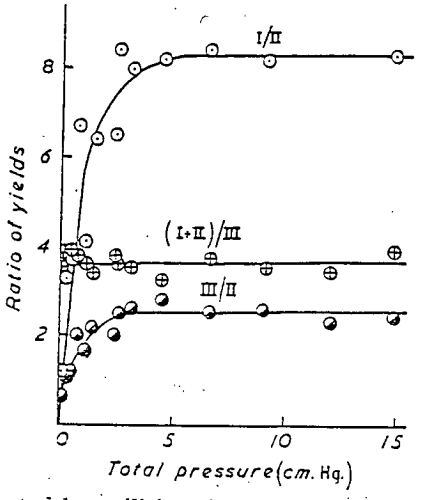
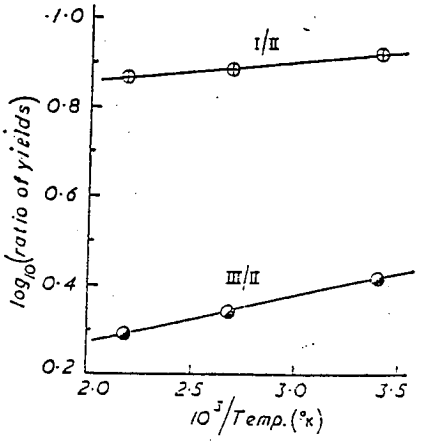


Fig. 2.



deactivated by collision, *i.e.*, $k_{1a}[M] \gg k_{1b}$. At the higher pressures, therefore, the values of the relative yields give the ratios of the rate constants k_1, k_2, and k_3. The effect of temperature on the high-pressure ratios is shown in Fig. 2. The straight lines have the equations:

$$k_1/k_2 = 6{\cdot}0 \exp [+ 180 \text{ cal. mole}^{-1}/RT]$$
$$k_3/k_2 = 1{\cdot}2 \exp [+ 430 \text{ cal. mole}^{-1}/RT]$$

Addition to the double bond is several times more rapid than insertion into the C–H bonds. This is in agreement with Frey [1] who showed that for ethylene $k_1/k_2 = 1{\cdot}6$, after allowance for 4 ethylenic bonds in ethylene and only two in *iso*butene. Skell and Woodworth's results [2] on the reaction of methylene with *cis*-but-2-ene and Skell and Garner's [3] on the reactions of CBr_2 with olefins in general confirm the conclusion.

The small activation-energy differences are of the same order as those previously found for insertion of CH_2 into saturated hydrocarbons.[4] They likewise fall in an unexpected order in that $E_{CH_2} > E_{C=O} > E_{CH_3}$. However, their absolute values are

probably low and are likely to be determined by steric requirements rather than by the strengths of the bonds broken or formed. The A factor ratios can be expressed in terms of the rates of attack on individual bonds as

$$A_{C=C} : A_{CH_2} : A_{CH_3} = 12 : 1{\cdot}00 : 0{\cdot}4 .$$

showing that the high reactivity of the double bond is due to a high entropy of activation, not to a low energy of activation. Skell and Woodworth's finding [2] that the addition of CH_2 to *cis*-but-2-ene is stereospecific rules out the possibility that this high entropy is due to free rotation in the activated complex. Skell and Garner's results [3] on the reactions of CBr_2 show that its reactions are much more selective than those of methylene. Addition to *iso*butene is, for example, some 14 times as fast as the addition to hex-1-ene, whereas preliminary results with methylene indicate that its addition to *iso*butene and pent-1-ene occur at roughly the same rate.

At low pressures, as seen from Fig. 1, the ratios I/II and III/II fall as the pressure is reduced while (I + II)/III remains constant. Compounds (I) and (II) are, therefore, alternative final products, the latter being increasingly favoured at lower pressures. This is in full accord with the scheme outlined above, where activated 1 : 1-dimethyl*cyclo*propane either isomerises [to (II)] or is stabilised by collision. The limiting pressure for stabilisation (about 4 cm.) may be compared with the corresponding pressure for activated *cyclo*propane [5] (about 200 cm.) and methyl*cyclo*propane [6] (about 40 cm.) formed by similar reactions of methylene with ethylene and propene. The larger number of degrees of freedom in the more complex activated molecules account for their greater lifetimes.

The isomerisation of (I*) might yield either 2-methylbut-2-ene (II) or 3-methylbut-1-ene (IV). Small quantities of the latter which has a boiling point close to that of the cyclic compound (I) might not have been detected on the chromatograms, and since the infrared identification was carried out with a sample from a high-pressure experiment, there is no direct analytical evidence that the but-1-ene was not formed at low pressures. However, the yield of (I + II) closely approaches zero at low pressures and so the percentage of the but-1-ene (IV) which could have been included in the analysis as dimethyl*cyclo*propane (I) must be low. Furthermore, the standard free-energy change ($\Delta F°$) for the conversion of (II) into (IV) is $\Delta F° = +3{\cdot}61$ kcal. mole^{-1} and if the isomerisation yields the methylbutenes (II) and (IV) in equilibrium proportions only $2{\cdot}4 \times 10^{-3}$ of the product will be the latter.

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Slow Oxidation of Ethane and Ethylene in the Gas Phase

Part 1.—General Features at 362°C

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The kinetic and analytical features of the oxidation of ethane and ethylene at 362° are described. In the early stages of the oxidation of ethane, 80 % of the hydrocarbon consumed gives ethylene. In the intermediate stages the ethylene is itself oxidized. In the initial stages of the oxidation of pure ethylene over 80 % of the hydrocarbon consumed gives formaldehyde, and in the intermediate stages the formaldehyde is oxidized to carbon monoxide. The main molecular stages in the oxidation are therefore ethane, ethylene, formaldehyde, carbon monoxide, with water also being formed at the appropriate stages.

The kinetics of the ethane oxidation are similar to those of the propane oxidation and the autocatalysis of the reaction is probably due to the oxidation of formaldehyde. The slow start of the acceleration is in part due to the fact that the branching intermediate is not an initial product of the reaction.

The general nature of hydrocarbon oxidation reactions is discussed. It is concluded that the main reaction of alkyl radicals with oxygen at 300-400° is usually an abstraction reaction

$$C_nH_{2n+1}+O_2 = C_nH_{2n}+HO_2.$$

However, there is strong evidence that the HO_2 radical is unable to abstract H from ethane or most other hydrocarbons, and it is proposed that a key reaction in alkane oxidation is the conversion of HO_2 to OH. The reaction $2HO_2 = 2OH+O_2$ is suggested.

There is general agreement on the main experimental facts concerning the gas phase oxidation of fuels. The reactions are usually autocatalytic and numerous intermediate products can be identified; the rates of oxidation of most fuels show a negative temperature coefficient between 300 and 400°C with the associated phenomenon of cool flames; the overall rates of oxidation of single fuels are very sensitive to their structure but their relative rates of oxidation in mixtures are much less so. These facts demand a free radical chain mechanism for their explanation.

Three distinct types of chain mechanism have been proposed for the oxidation of alkanes (and more generally saturated fuels). These are the peroxide,[1-3] the aldehyde [4, 5] and the olefin mechanisms.[6, 7] All accept that the primary product from free radical attack on an alkane is an alkyl radical; they differ primarily in the mode of oxidation of the alkyl radical. With ethyl, e.g., the theories give:

peroxide
$$C_2H_5+O_2 = C_2H_5OO \quad (1)$$
$$C_2H_5OO+C_2H_6 = C_2H_5OOH+C_2H_5. \quad (2)$$

aldehyde
$$C_2H_5+O_2 = CH_3CHO+OH, \quad (3)$$

olefin
$$C_2H_5+O_2 = C_2H_4+HO_2. \quad (4)$$

The first two mechanisms were supported by the evidence of peroxides and aldehydes in the reaction products. However, in the early stages of alkane oxidations the major initial product is an olefin [8, 9] with the same number of carbon atoms as the alkane. As this reaction accounts for about 80 % of the alkane disappearing, the peroxide and aldehyde mechanism cannot account for more than about 20 % of

the oxidation at most. The evidence now presented shows that for ethane reactions (2) and (3) are unimportant above about 320°.

Apart from the olefin, in the early stages the combined yield of H_2O_2 and H_2O is close to that of the olefin. The peroxide yield is usually about 30 % that of the water.[10, 11] For ethane, the overall initial reactions thus appear to be

$$C_2H_6+O_2 = C_2H_4+H_2O_2 \quad (5)$$

and

$$C_2H_6+\tfrac{1}{2}O_2 = C_2H_4+H_2O. \quad (6)$$

Hydrogen peroxide could arise from two reactions

$$2HO_2 = H_2O_2+O_2 \quad (7)$$

$$HO_2+C_2H_6 = H_2O_2+C_2H_5. \quad (8)$$

Reaction (7) is important in the oxidation of hydrogen at 500° in boric acid coated vessels.[12] At this temperature the peroxide quickly dissociates and the reaction proceeds by means of a " degenerate chain " in which free radical and molecular intermediates alternate as active species. Sampson [13] has shown convincingly that a similar mechanism applies in the oxidation of ethane at 600°. The degenerate chain for both systems can be written

$$OH+C_2H_6(H_2) = H_2O+C_2H_5(H) \quad (9)$$

$$C_2H_5(H+M)+O_2 = C_2H_4(M)+HO_2 \quad (4)$$

$$2HO_2 = H_2O_2+O_2 \quad (7)$$

$$H_2O_2+M' = 2OH+M' \quad (10)$$

(the reactants and products in brackets apply to the hydrogen+oxygen reaction). The overall rates of both reactions are close to the independently measurable rate of homogeneous pyrolysis of the hydrogen peroxide present. At 300°, however, the rate of pyrolysis of the peroxide is much too low,[14] so that reaction (7) cannot be the main remover of HO_2 if the overall oxidations are chain reactions. There are, however, serious objections to reaction (9) since D[H—OOH] = 89±2 kcal.[15] Therefore most reactions of HO_2 with alkanes will be endothermic and are likely to have activation energies at least 5 kcal greater than their endothermicities. Falconer, Knox, Smith and Trotman-Dickenson [16, 17] found that the relative rates of oxidation of propane and ethane in mixtures of two hydrocarbons differed by a factor of 2·3. The relative rates of attack of Cl[18], CH_3O[14] and Br[18] on these hydrocarbons are 2·0, 3·0 and 10 at 350°C. Consequently on the basis of these experiments *taken only* OH [19] is the most likely attacking radical. There is good evidence for the unreactivity of HO_2 in the hydrogen-oxygen reaction [12] and in the methane oxidation.[20] The dependence of the rate of slow oxidation of hydrogen on the hydrogen mole fraction at 500° requires the introduction of a " regeneration reaction ":

$$HO_2+H_2 = H_2O_2+H. \quad (11)$$

Although the HO_2 concentration must be much higher than the OH concentration this reaction never accounts for more than 5 % of the hydrogen consumption. From the overall rate of the reaction and assuming reactions (7) and (11) have steric factors of unity, E_{11} is calculated to be about 27 kcal. If the steric factor of (11) were 10^{-3}, E_{11} = 17 kcal.

In the oxidation of methane,[20] the formaldehyde concentration passed through a maximum during the reaction. This maximum increased with temperature with

an activation energy of about 8 kcal. According to their mechanism [20] this energy is given by

$$E_F = \tfrac{1}{2}\{E(HO_2+CH_4)+E(OH+CH_4)-E(HO_2+CH_2O)-E(OH+CH_2O)\}.$$

Since the activation energies of the two OH radical reactions are probably low the difference in the activation energies of the HO_2 radical reactions must be close to 16 kcal and thus $E(HO_2+CH_4)\gtrsim 16$ kcal. These values for $E(HO_2+H_2)$ and $E(HO_2+CH_4)$ compare with 20 and 18 kcal for the corresponding reactions of bromine atoms.[18] It is therefore likely that $E(HO_2+C_2H_6)\approx 13$ kcal. It is most unlikely that the competitive experiments can be explained on the basis of HO_2 as the radical attacking the hydrocarbons. Since the formation of HO_2 along with the olefin in reaction (4) seems unavoidable, a key reaction in hydrocarbon oxidation may be the conversion of HO_2 to OH. The most plausible reaction is

$$2HO_2 = [HOO—OOH] = 2OH+O_2. \qquad (12)$$

This reaction is analogous to those of alkyl peroxy radicals to give alkoxy radicals + oxygen,[21, 22] but whereas the latter are almost certainly exothermic since they occur at room temperature, reaction (12) is about 8 kcal endothermic. The difficulty of the endothermicity can be overcome if it is supposed that the hydrogen tetroxide is a true intermediate which decomposes preferentially to OH and O_2 rather than to HO_2. The decomposition into three fragments might be expected to have an A factor higher by between 10^2 and 10^3, which could compensate for the adverse activation energy.[23]

The initial aim of the present work was to discover whether ethane, the simplest hydrocarbon showing all the characteristics of higher alkane combustion,[24] was oxidized initially to ethylene, acetaldehyde or ethyl hydroperoxide above 320°, and to establish the main products of oxidation of ethyl between 300 and 400°C. We have shown that ethylene indeed accounts for about 80 % of the initial products with formaldehyde as a minor product. The concurrent study of the oxidation of ethylene has shown that its main initial oxidation product is formaldehyde (>80 %) with ethylene oxide as a minor product. The main molecular stages of the oxidation of ethane are thus:

$$\underset{}{\text{ethane}} \rightarrow \underset{+\text{water}}{\text{ethylene}} \rightarrow \underset{+\text{water}}{\text{formaldehyde}} \rightarrow \text{carbon monoxide}$$

The results agree with Gray [6] and with Steacie and Plewes [25] as regards the production of ethylene and with Bone and Hill [26] who established the main oxygenated products. They also fall into line with the work of Sampson [13] on the ethane oxidation at 600°C and that of Dingledy and Calvert [22] on the oxidation of ethyl radicals at room temperature.

EXPERIMENTAL

MATERIALS

Oxygen was taken directly from B.O.G. cylinders and dried by bubbling through liquid oxygen. It contained 0·3 % nitrogen. Ethane, supplied by B.O.G., contained 1·5 % ethylene which was removed by passing the gas through a column of charcoal saturated with bromine. Any bromine carried over from this column was absorbed by N : N-dimethyl p-toluidine supported on firebrick. The ethane was dried by passage through a trap at −80°C and collected at −183°C. It was finally subjected to several trap-to-trap distillations, first and last fractions being rejected. Ethylene, supplied by B.O.G., contained 1·5 % carbon dioxide as the only detectable impurity.

APPARATUS

The reaction was carried out under static conditions in a 500 ml Pyrex reaction vessel 5·5 cm diam. housed in an electric furnace whose temperature was constant and uniform to about 1 deg. Reaction mixtures were made up in a mixing vessel to the required composition. The reaction was followed by measurement of pressure change with a Pyrex-glass spoon gauge fitted with an all-glass link system which moved a small mirror. A light spot reflected by the mirror moved 5·30 cm on a scale for each cm Hg pressure difference.

ANALYSIS

The analysis of reaction products was carried out wherever possible by gas chromatography. Eluted components were identified by comparison of their retention times with those of pure substances and where possible by their infra-red spectra. Infra-red identification required about 10^{-6} moles of sample. Formaldehyde and hydrogen peroxide were analyzed colorimetrically. The sampling system consisted of two 25 ml traps which could be simultaneously connected to the reaction vessel. Both sampling vessels and the connecting tubing were heated to prevent condensation of water vapour. The sample in one of the traps was analyzed for formaldehyde or hydrogen peroxide and that in the other by gas chromatography for the remaining products. The sharing ratios between the two sampling vessels and the reaction vessel were known and absolute measurements of the quantities of the various products present in the sample volumes enabled their pressures in the reaction vessel to be determined. Calibration of the gas chromatograph was accordingly carried out on an absolute basis.

The formaldehyde was determined by the chromotropic acid method [27] and the hydrogen peroxide by the titanium sulphate method.[28] No analysis was made for other peroxides which, from Cartlidge and Tipper's [29] work and our own carbon balances, were assumed to be absent. Formic and acetic acids [26] were not detected by gas chromatography. Since hydrogen peroxide analyzed as water, the yields of water refer to $H_2O + H_2O_2$.

GAS CHROMATOGRAPHIC ANALYSIS

The contents of the trap for gas chromatographic analysis were divided into three fractions (*a*) gases uncondensed at −183°C, (*b*) products involatile at −183° but volatile at −80° and (*c*) the remaining products termed " the condensables ". The quantities of (*a*) and (*b*) were separately measured in a calibrated gas burette fitted to a Toepler pump, and aliquots were transferred to the sampling U-tube of the gas chromatography apparatus. From the gas chromatograms subsequently obtained the proportions of each component were obtained and hence their partial pressures in the reaction vessel. Absolute determination of the amounts of components present in the aliquots agreed well with the total quantities of sample indicating that no component in fractions (*a*) or (*b*) was missed. The condensables were completely transferred to the U-tube of the chromatography apparatus and an absolute quantitative analysis carried out. The columns employed for the analysis of the three fractions are given in table 1. Detection was by katharometer and the carrier gas was hydrogen.

The low temperature column used for the separation of ethylene, carbon dioxide and ethane was ideal since ethylene was eluted before ethane and trace quantities could readily be determined. Acetylene was eluted before ethylene and none could be detected in the oxidation products of ethylene.

The analysis of fraction (*c*) was complicated: (i) owing to the slight volatility of ethylene oxide and acetaldehyde at −80° small quantities of these substances were usually present in fraction (*b*) and it was always necessary to analyze an aliquot of this fraction on column 4. (ii) Since acetaldehyde and ethylene oxide were not separated on column 3, the first peak containing these components was trapped in a spiral packed with glass beads and cooled to −183°. After their elution the trap was by-passed for the rest of the analysis. The contents of the spiral were then analyzed on column 4. (iii) Water was eluted from column 3 long after ethanol. To obtain analysis with reasonable sensitivity the second half of

TABLE 1.—GAS CHROMATOGRAPHIC COLUMNS

column	fraction	container	length cm	support	liquid phase	temp. (flow rate ml min^{-1})	substances analyzed
1	*a*	glass U	150	Linde molecular sieve 5A + activated charcoal		18°C (30)	O_2, (N_2), CO, CH_4
2	*b*	copper coil	300	Celite 60-80 mesh	20 % 140-160°C petroleum	−80°C (30)	(C_2H_2) CO_2, C_2H_4 C_2H_6
3	*c*	glass U	150	Celite 60-80 mesh	20 % polyethylene glycol 400	47°C (70)	condensables *
4	*c*	copper coil	150	same as column 3		0°C (70)	CH_3CHO, C_2H_4O

* Condensables in order of elution were $CH_3CHO + C_2H_4O$, CH_3OH, C_2H_5OH and H_2O.

column 3 was disconnected after the elution of the alcohols and the water eluted from the first half of the column only. (iv) Acetaldehyde condenses with hydrogen peroxide [30] and the gas chromatographic determination of acetaldehyde in the presence of hydrogen peroxide would be expected to be low. Tests in which solutions of acetaldehyde in 30 % hydrogen peroxide were analyzed on column 4 showed that only about 1/7th of the acetaldehyde was eluted as such. However, by coating the walls of the sampling vessel with barium hydroxide, about 95 % of the aldehyde was recovered. When the coated sampling vessel was used for oxidation products the yield of acetaldehyde rose by only 30 %. Thus, the heating and cooling of the sample must have been so rapid that no appreciable reaction of aldehyde with peroxide could take place.

RESULTS

Kinetic experiments were carried out at 362°. Analytical experiments were carried out on seven ethane-oxygen mixtures between 318 and 386°, one ethane + ethylene + oxygen mixture at 362° and three ethylene + oxygen mixtures at 318 and 362°. Details are given in table 2.

TABLE 2.—MIXTURES STUDIED

mixture [a]	components	molar composition	total pressure mm Hg	temp. °C	notes
2E31	ethane + oxygen	3 : 1	296	318	
2E11	" "	1 : 1	442	318	
4E11	" "	1 : 1	442	340	*b*
6E31	" "	3 : 1	296	362	
6E11	" "	1 : 1	442	362	*c*
6E12	" "	1 : 2	442	362	
8E11	" "	1 : 1	442	386	*b*
6EA11	ethane + ethylene + oxygen	6·3 : 1 : 7·3	442	362	
2A11	ethylene + oxygen	1 : 1	442	318	
6A11	" "	1 : 1	441	318	
6A12	" "	1 : 2	333	362	*b*

(*a*) The first number in the code gives the approximate oxidation temperature in tens of degrees above 300°; the letters E and A denote ethane and ethylene respectively; the final two figures give the hydrocarbon to oxygen ratio.
(*b*) reaction products analyzed only in the initial stages.
(*c*) reaction studied with and without the addition of 1 % acetaldehyde.

KINETIC FEATURES

The oxidations of both ethane and ethylene are autocatalytic.[26, 31] Typical pressure against time curves are shown in fig. 1*a*.

In the oxidation of ethane the pressure rise Δp is proportional, except in the last stages of reaction, to the amount of water formed and to the consumption

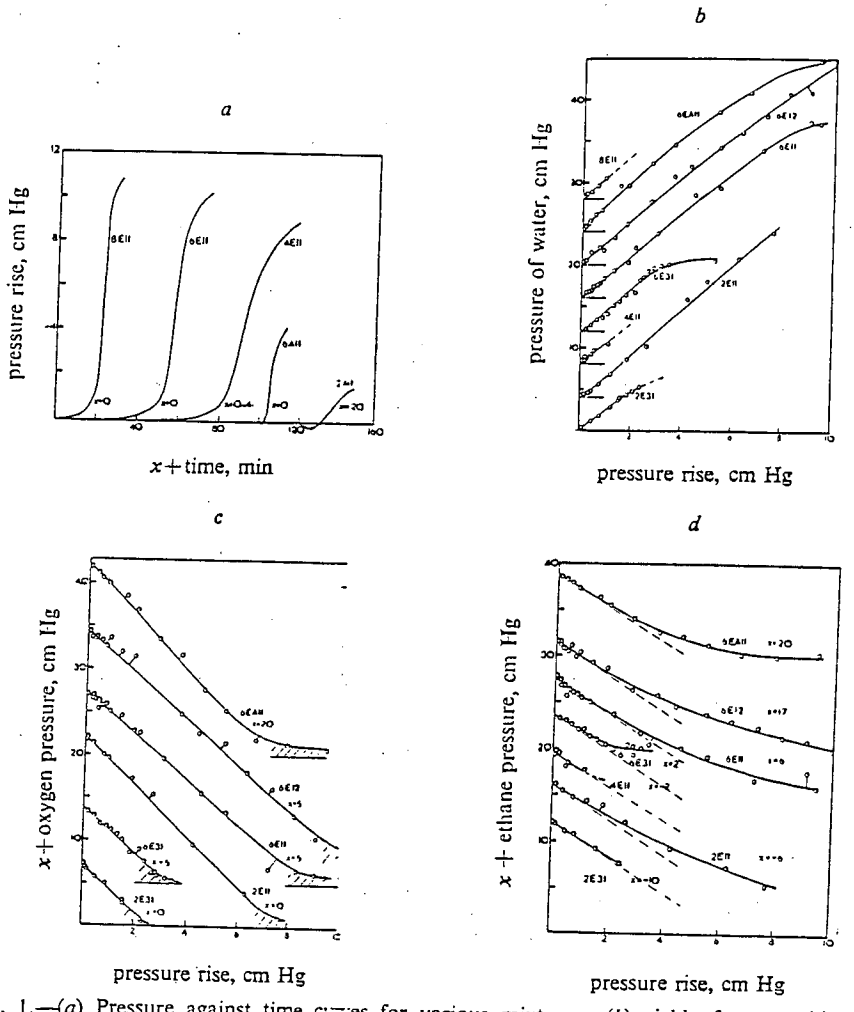

FIG. 1.—(*a*) Pressure against time curves for various mixtures; (*b*) yield of water; (*c*) oxygen pressure and (*d*) ethane pressure as functions of pressure rise. For key to mixture compositions and temperatures see table 2.

of oxygen (fig. 1*b* and 1*c*). The proportionality constants (except for the ethane + ethylene + oxygen mixture) are independent of composition at any temperature. Thus, pressure rise can be used to measure the extent of reaction for the greater part of the reaction. The proportionality between pressure rise and water production is independent of temperature as well as composition:

$$d[H_2O]/d\Delta p = 2{\cdot}6,$$

but that between pressure rise and oxygen consumption falls with rise of temperature,

$$d[O_2]/d\Delta p = 3{\cdot}0 \text{ at } 318° \text{ and } 2{\cdot}6 \text{ at } 362°.$$

Initially ethane is consumed at about twice the rate of pressure rise (fig. 1*d*) but later because of oxidation of the initial products the rate of consumption falls. In fig. 1*d* the broken lines have been drawn with an initial gradient

$$d[C_2H_6]/d\Delta p = 2{\cdot}0.$$

The initial gradients are similar to those obtained for the oxidation of propane at 318°.[8]

The pressure against time curves for ethane (fig. 1*a*) are sigmoid and at low temperatures and pressures the reaction exhibits an induction period. Generally oxidation reactions accelerate exponentially during the initial stages, i.e.,

$$\Delta p = A \exp(\phi t) \quad \text{or} \quad d\Delta p/dt = \phi \Delta p.$$

However, the plot of reaction rate against pressure rise (fig. 2*a*) shows that the acceleration gradually increases from nearly zero to a maximum value which is held almost until the maximum rate of reaction is achieved. Thereafter the reaction slows down at a rate which is greater the less oxygen is present. The period of increasing acceleration, ringed in fig. 2*a*, was also noted with propane[7] and found to be highly susceptible to the addition of inert gases. During this period some reactive species is efficiently removed on the walls of the reaction vessel. Later, the walls are less effective judged by the same criterion. This may be because the walls become acclimatized during the reaction or because the mechanism of the reaction changes.

The maximum acceleration constant, measured from the straight parts of plots like that in fig. 2*a*, increases rapidly with ethane pressure at 362° with an order much higher than unity (fig. 2*b*). The dependence is similar to that found with isobutane at 318°[32] but contrasts with that found for ethane and propane at this temperature when ϕ increased linearly with hydrocarbon pressure above a certain limiting pressure.[7, 32] With increasing oxygen pressure, ϕ increases linearly at first but becomes independent of oxygen pressure when it exceeds the ethane pressure. This behaviour has been noted with other hydrocarbons.[7, 33] Inert gas (carbon dioxide) has a slight catalytic effect. This contrasts with the marked effect noted with propane in the early part of the reaction and indicates that diffusion-controlled processes are important in the early stages only.

Replacement of part of the ethane by ethylene (fig. 2*c*) increases the maximum acceleration constant considerably and ethylene is thus a promoter of the reaction as is propylene in the oxidation of propane.[7] The effect of ethylene partly explains the maintenance of the acceleration constant in spite of the consumption of the reactants since ethylene accumulates during the reaction. Replacement of ethane by ethylene oxide has no effect on ϕ and the addition of ethylene oxide has the same effect as the addition of an equal amount of ethane. Ethylene oxide is therefore neither a promoter nor a branching agent. It has much the same reactivity as ethane in the oxidizing mixture.

Acetaldehyde is a catalyst of gas-phase oxidations and is often suggested as a degenerate branching agent. Its addition to a mixture of ethane and oxygen (fig. 2*d*) considerably reduces the induction period but even a 4 % addition (based on the ethane pressure) does not eliminate the period of autocatalysis. Approximately 1 % (2 mm pressure) is required to reduce the induction period substantially but this is about ten times the maximum quantity of acetaldehyde found by analysis at 362°. It therefore seems unlikely that acetaldehyde is an important branching agent in the oxidation of ethane.

The oxidation of ethylene differs from that of ethane in starting with a pressure decrease at 362° and below. The pressure decrease is more pronounced the lower the temperature, and has been noted with other olefins.[34-36] Pressure change cannot therefore be used as a measure of the extent of reaction and the only simple way of studying the kinetics is by an analytical method. There is even some doubt as to whether the reactions are truly autocatalytic at the lowest temperatures.

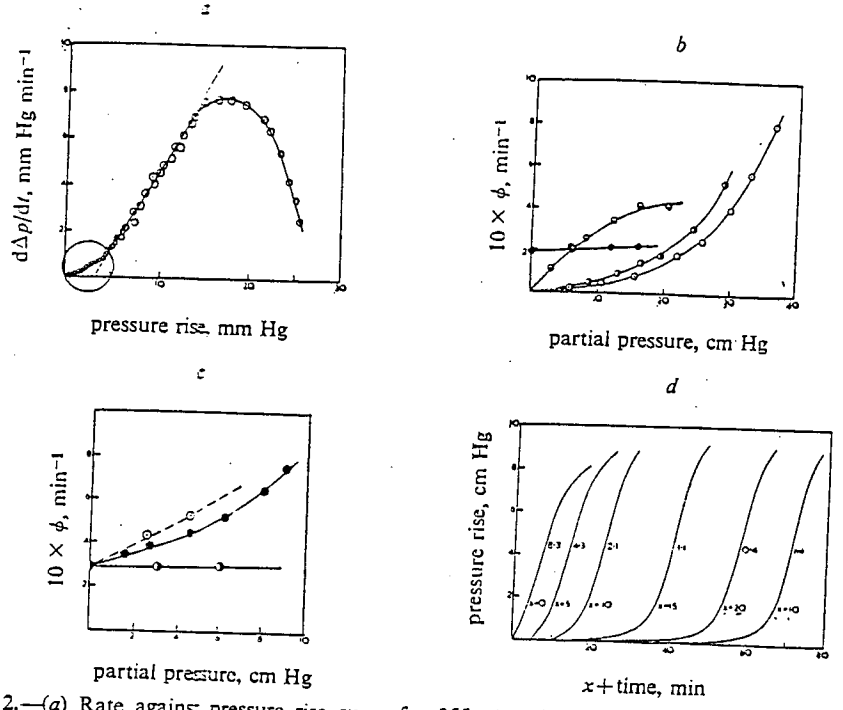

FIG. 2.—(*a*) Rate against pressure rise curve for 355 mm ethane+90 mm oxygen at 362°; ϕ = 0·35 min^{-1}; (*b*) variation of ϕ with reactant pressure at 362°. ⊙ 7·7 cm oxygen, ethane varied; ◑ 15·3 cm oxygen, ethane varied; ◒ 25·6 cm ethane, oxygen varied; ● 21·8 cm ethane, 7·7 cm oxygen, carbon dioxide varied; (*c*) variation of ϕ, mixture 6E11. ● ethylene substituted for ethane; ◑ ethylene oxide substituted for ethane; ⊙ ethylene oxide added; - - - ethane added (from fig. 2*b*). (*d*) Effect of added acetaldehyde on pressure time curves: pressures of added acetaldehyde in mm are marked on lines, mixture 6E11.

GENERAL ANALYTICAL FEATURES

In order to elucidate the reactions occurring at various stages in the oxidation it is necessary to carry out detailed analyses and it is desirable to plot the yields of the products against some measure of the extent of reaction. The lines for true initial products then start from the origin at a finite angle to the X-axis whereas those of secondary products start tangential to the X-axis.

There are several possible measures of the extent of reaction. Pressure rise is the simplest but may be in error in the earliest stages either because of small temperature fluctuations or because of uncertainty in the mechanism in a region where pressure change cannot be accurately correlated with consumption of reactants. Furthermore, it can only be used for alkane oxidations since the olefin oxidations start with pressure decreases. The consumption of hydrocarbon or oxygen is the only true measure of the extent of reaction but analytical techniques at present

available are not sufficiently accurate to measure very small consumptions. The yield of some major product such as water is satisfactory if it is known to follow the consumption of one or other of the major reactants. In presenting the overall results and those for the final stages this parameter is the most convenient, but is not ideal for the initial stages firstly because the analysis of traces of water by gas chromatography is difficult and secondly because water is not a major initial product of the oxidation of ethylene. For this region the quantity of carbon found by analysis in the products is undoubtedly the best measure of extent of reaction, provided that the carbon balances are close to 100 %. Generally throughout the work this was the case. Only for the ethane+ethylene+oxygen mixture (6EA11) was there a systematic discrepancy and therefore the reaction in the initial stages could not be satisfactorily examined. This measure of the extent of reaction is unfortunately not applicable to the final stages of the reaction since they involve mostly the oxidation of products and the total carbon in the products is therefore nearly constant even when oxidation continues to occur.

The general analytical features of all mixtures were similar and are illustrated in outline for equimolar ethane+oxygen and ethylene+oxygen mixtures at 362° (mixtures 6E11 and 6A11) in fig. 3*a* and 3*b*. Ethane and ethylene give the same oxidation products although in different proportions, and their oxidations are closely interrelated. The data for acetaldehyde are not included in the figure since the maximum concentration recorded at 362° was 0·2 mm.

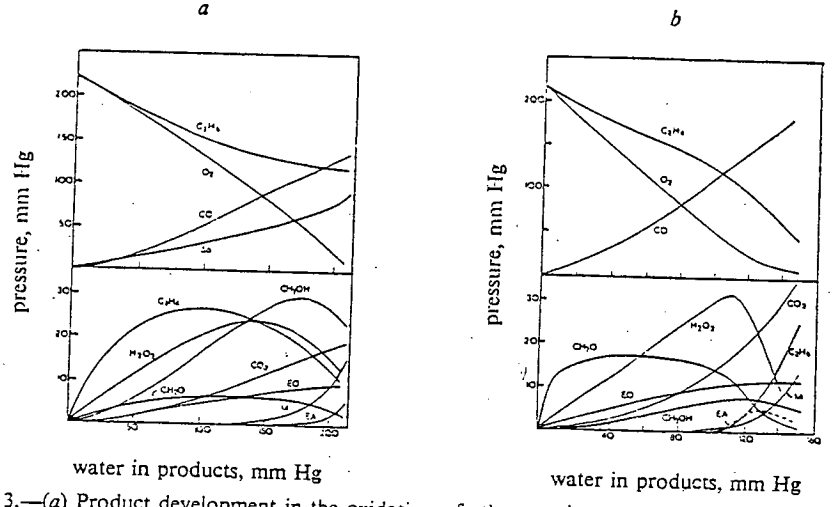

FIG. 3.—(*a*) Product development in the oxidation of ethane, mixture 6E11. (*b*) Product development in the oxidation of ethylene, mixture 6A11. EO = ethylene oxide, M = methane, EA = ethanol.

Ethylene and an equivalent amount of water+hydrogen peroxide are the chief initial products of the oxidation of ethane; and formaldehyde alone is the chief initial product of the oxidation of ethylene. The yields of both ethylene and formaldehyde pass through maxima indicating their consumption in the later stages of the oxidations. Since carbon monoxide and water are the main oxidation products of formaldehyde [37, 38] the molecular stages in the oxidation of ethane must be:

$$C_2H_6 \xrightarrow[a]{+O_2} C_2H_4 \xrightarrow[b]{+O_2} 2CH_2O \xrightarrow[c]{+2O_2} 2CO$$

with water and hydrogen peroxide being formed in appropriate amounts in stages (*a*) and (*c*). The initial yield of hydrogen peroxide from both ethane and ethylene oxidations was about 30 % that of the water+peroxide. As the yield of peroxide did not fall off until near the end of the reaction, it seems likely that heterogeneous decomposition was not of major importance, and that the figure of 30 % represents the true proportion of peroxide formed in the reaction.

Minor initial products were formaldehyde from the oxidation of ethane, and ethylene oxide from the oxidation of ethylene. Methanol as shown in part 2 was not an initial product of either oxidation; it was formed in greater yield in the oxidation of ethane and therefore cannot be a secondary product formed through the agency of ethylene. Its most likely free-radical precursor is methoxy. Ethylene oxide appears to be formed only by oxidation of ethylene and not as an initial product from the ethane oxidation in agreement with Sampson's work at 600°C.[13]

Methane and ethanol appear towards the end of both oxidations, and ethane appears at the end of the oxidation of ethylene. These products suggest the prior formation of methyl, C_2H_5O and ethyl. Certain deductions may be made about reactions involving these radicals.

METHOXY.—If methanol is derived from methoxy and if methoxy is an initial product of the oxidation it must be largely oxidized to formaldehyde in the early stages. Only when a good hydrogen donor such as formaldehyde, has accumulated can abstraction compete with oxidation. The precursor of methanol is unlikely to be hydroxymethyl since it has a lower heat of formation [39] and its abstraction reactions would mostly be endothermic. Oxidation would probably be the preferred reaction.

C_2H_5O.—Ethanol is formed in the last stages of the oxidations at 362° when the oxygen concentration is low. This suggests that a competition may take place between oxidation of and abstraction by C_2H_5O. However, the likely oxidation products are acetaldehyde and ethylene oxide.[11] Since both are formed in relatively small proportions, too small to be regarded as substitutes for ethanol, it seems that the C_2H_5O radical is peculiar to the final stages of the reaction.

METHYL.—The most likely source of methyl is the decomposition of the ethoxy radical which has an activation energy of about 17 kcal.[39] The formation of ethanol and methane may therefore be closely connected. Both may derive from the ethoxy radical.

ETHYL.—The formation of ethyl in the ethylene oxidation strongly suggests that reaction (4) is reversible and that when the oxygen concentration is low the equilibrium

$$C_2H_4+HO_2 = C_2H_5+O_2 \qquad (-4)$$

is sufficiently displaced to the right that abstraction by ethyl can take place from substances with weak C—H bonds such as formaldehyde and methanol.

DISCUSSION

The analytical data presented strongly suggest that the main reactions removing ethane are

$$C_2H_6+X = C_2H_5+XH \qquad (13)$$

$$C_2H_5+O_2 = C_2H_4+OH_2, \qquad (4)$$

with about 5 % of the reaction occurring by

$$C_2H_5+O_2 = CH_2O+CH_3O \qquad (14)$$

$$CH_3O+O_2 = CH_2O+HO_2. \qquad (15)$$

The oxidation of ethylene produces formaldehyde and a small proportion of ethylene oxide. HO_2 will be formed both in the oxidation of ethane by (4) and in the oxidation of ethylene through the concurrent oxidation of formaldehyde by reaction (16),

$$CHO + O_2 = CO + HO_2. \quad (16)$$

Because it is a relatively unreactive radical it is likely to be present in rather high concentration. The major reaction of ethylene is therefore likely to be addition to HO_2:

$$C_2H_4 + HO_2 = CH_2 . CH_2 . OOH \quad (17)$$

$$CH_2CH_2OOH = CH_2O + CH_2OH \quad (18)$$

$$CH_2OH + O_2 = CH_2O + HO_2, \quad (19)$$

followed by decomposition of the peroxy radical and finally oxidation of the hydroxymethyl radical. The formation of ethylene oxide is readily explained by the " planting " of an O atom by HO_2 on to the ethylene molecule,

$$HO_2 + C_2H_4 = C_2H_4O + OH. \quad (20)$$

It is unlikely to be formed via 3-membered-ring transition states from C_2H_5OO or C_2H_4OOH.

In the ethane oxidation the further oxidation of the ethylene initially formed is therefore the main source of formaldehyde. Near the point of maximum reaction rate the ethylene and formaldehyde concentrations are stationary and therefore both formaldehyde and ethylene must be undergoing oxidation at nearly the same rate as the ethane (slightly less because not all the ethane yields ethylene and not all the ethylene yields formaldehyde as initial products). The relative ease of oxidation of ethane, ethylene and formaldehyde must therefore be roughly in inverse proportion to their concentrations at this point in the reaction. The relative reactivities are then : ethane 1·0, ethylene 5, and formaldehyde 20. If a single radical is responsible for the attack on these three substances then these figures represent relative rate constants (see, e.g., ref. (40)).

Hydroperoxides are probably important as the degenerate branching intermediate below about 300° while aldehydes are more important above this temperature.[29] In the oxidation of ethane, acetaldehyde is only a trace product and the low catalytic activity of added acetaldehyde rules it out as the major autocatalyst at 362°. Ethylene oxide, a possible autocatalyst in the ethylene oxidation above 400°,[31] is not a catalyst in the ethane oxidation at 362° as shown by its negligible effect on the acceleration constant when added in substantial quantity. Hydrogen peroxide has little catalytic effect on oxidations[41-43] even when it is probably pyrolyzing homogeneously at a considerable rate. Methanol does not itself oxidize below about 400°.[44] Thus formaldehyde which oxidizes above 270°[45] remains the only reasonable possibility. It is unfortunate that the catalytic effect of formaldehyde was not investigated in the present study. Since formaldehyde is formed mainly from ethylene and not directly from ethane the slow start of the ethane oxidation can be partly explained. The failure of acetaldehyde to remove the autocatalysis even when in considerable concentration is likewise explained since the reaction can only proceed at maximum rate when both ethylene and formaldehyde have accumulated. This requires a substantial amount of reaction, considerably more than that induced by the oxidation of the added acetaldehyde. In working out the kinetics of a reaction where the degenerate branching intermediate is essentially a secondary product the assumption that the maximum reaction rate can be achieved with insignificant consumption of the fuel is untenable. In the

oxidation of ethylene this situation does not arise and Harding and Norrish could completely remove the induction period and autocatalysis of the reaction by the addition of sufficient formaldehyde to the mixture.

We therefore conclude that the oxidation of ethane and possibly other alkanes is not a simple degenerately branching chain reaction [46] but one in which the branching intermediate is a secondary product of the oxidation. This fact probably accounts for the promoting effect of olefins on the oxidation of alkanes. The kinetics of this type of reaction are more complicated than those of a simple degenerately branching chain reaction and the apparent exponential acceleration over much of the reaction may result simply from the balancing of a number of compensatory factors.

The high order of acceleration constant with respect to ethane concentration probably reflects this complexity since the build-up of formaldehyde results from two consecutive processes. The independence of the acceleration constant on oxygen pressure in fuel-weak mixtures is in line with the analytical data presented later that oxygen concentration has little effect on the relative yields of important products. It therefore appears to have little kinetic role in oxidations and its major role is to add to, or abstract from radicals in processes which are not rate determining.

We have avoided discussion of the nature of the species X in reaction (13). The relative reactivities of the C—H bonds in ethane and formaldehyde are approximately 1 : 7 as deduced from the concentrations of the two species when the formaldehyde concentration is a maximum. If we assume that the same radical attacks formaldehyde as ethane and that the A factors per C—H bond are equal the activation energy for attack of X on ethane is about 2 kcal greater than for attack on formaldehyde. This is a small difference when it is taken with the relative bond strengths in ethane and formaldehyde and suggests that X, if a single species, is much less selective than HO_2. Enikolopyan and co-workers [19] suggested that activation energy difference for HO_2 attack on methane and formaldehyde is about 16 kcal. In the ethane oxidation it therefore seems more likely that the ethane is removed predominantly by OH radical attack and the formaldehyde by HO_2 radical attack. Thus the conversion of HO_2 to OH is required on the basis of internal evidence.

Further support for this is found in the contrasting effects of inert gas on the induction period and the main part of the reaction. Reaction (12) for the conversion of HO_2 to OH is second order in HO_2 and will therefore only occur when the concentration of HO_2 is high. In the absence of mutual reaction of HO_2 radicals by (7) or (12) the radicals will tend to diffuse to the walls of the reaction vessel possibly attacking a small number of C_2H_6 molecules on the way. Thus we might expect a diffusion controlled chain reaction in the initial stages which becomes a gas phase terminated chain reaction in the later stages when the rate of reaction has risen sufficiently.

The time of diffusion of HO_2 to the walls in the present reaction vessel is about 0·5 sec (see ref. (46)) and the rate constant of reaction (8) is probably given approximately by

$$k_8 = 10^9 \exp[-13{,}000/RT] \text{ mole}^{-1} \text{ l. sec}^{-1}$$
$$= 10^{+4.5} \text{ mole}^{-1} \text{ l. sec}^{-1} \text{ at } 635°\text{K}.$$

The chain length with an ethane concentration of 200 mm (5×10^{-3} mole l.$^{-1}$ at 635°K) is then about 90.

As the reaction accelerates the concentration of HO_2 rises and eventually mutual reaction will occur. The chain length will then decrease due to reaction (7). When the chains are fully terminated in the gas phase inert gas will have no effect.

The importance of HO_2 attack on ethane may be assessed as follows. Let us assume that HO_2 is involved only in reactions (7) and (8). Baldwin [12] considers that $k_7 = 10^{10}$ mole^{-1} l. sec^{-1}, which is slightly less than the collision number. The maximum rate of removal of ethane in the 1 : 1 mixture at 362°C is 0·3 mm sec^{-1}. Denoting reaction rates by R_7, R_8, etc., we then have

$$0{\cdot}3 \text{ mm sec}^{-1} = R_8 = k_8[HO_2][RH],$$
$$R_7 = k_7[HO_2]^2,$$
$$R_7/R_8 = k_7R_8/(k_8[RH])^2,$$

with $k_8 = 10^{+4.5}$, $k_7 = 10^{10}$, $R_8 = 10^{-5}$ and $[RH] = 5 \times 10^{-3}$ (units being mole l.$^{-1}$ and sec), we obtain $R_7/R_8 = 3$. Recombination of HO_2 would therefore be expected to compete strongly with abstraction of HO_2 from ethane. The evidence is therefore that HO_2 chains cannot account for the observed rate of removal of ethane if they are properly terminated by reaction (7). If, on the other hand, the mutual reaction of HO_2 radicals occurs to some extent by reaction (12) then for every HO_2 which terminates the reaction by (7) there will be a number of OH radicals which will remove ethane. On the basis of the initial yield of H_2O_2 and water, k_{12}/k_7 cannot be greater than 2 or 3. Thus the chains are likely to be extremely short and for the reaction to show autocatalysis a strong branching reaction must be introduced. In an earlier paper [7] it was deduced that alkane oxidations proceeded by chains which provided only a few molecules of branching agent per chain; this was thought due to the small proportion of chain steps forming branching agent rather than to the shortness of the chains. It now appears that the second alternative may be correct for the main stages of the reaction although the first may be true during the induction period. There is indirect evidence that oxidation chains may be much shorter than generally thought. When hydrogen peroxide is added to methane + oxygen [42] and formaldehyde + oxygen [41] mixtures it has little catalytic effect even at temperatures where it should be decomposing at a substantial rate. This can be explained by supposing that the internal sources of new radicals produces them faster than the added material. Since the rate of generation of OH by hydrogen peroxide is in some cases a large fraction of the reaction rate the chains must be very short.[47]

We therefore conclude that the oxidations start as well-terminated chain reactions in which HO_2 is the chain carrier and where the chain length may be about 100 units, but that at a low percentage conversion, when the reaction rate is only just becoming measurable, wall reaction of HO_2 radicals is replaced by mutual reaction in the gas phase. Probably, the majority of the HO_2 radicals reacting in this way produce hydroxyl and oxygen directly not hydrogen peroxide as is generally supposed.

In proposing the conversion of HO_2 to OH by reaction (12) it is necessary to consider the effect of its introduction into the scheme for the hydrogen oxygen reaction. Baldwin *et al.*[12] have shown that the slow oxidation in boric-acid-coated vessels proceeds by a degenerate chain reaction comprising reactions (9), (4), (7) and (10), which in their notation are numbered (i), (iv), (x), and (vii). This scheme predicts that the overall rate of slow oxidation at pressures above the second explosion limit is close to the independently measurable rate of homogeneous decomposition of hydrogen peroxide, which is thought to occur by the reactions [14]

$$H_2O_2 + M' = 2OH + M' \qquad \text{(vii)}$$
$$OH + H_2O_2 = H_2O + HO_2 \qquad \text{(xv)}$$
$$2HO_2 = H_2O_2 + O_2 \qquad \text{(x)}$$

Thus the observed rate of pyrolysis of the peroxide is twice the rate of reaction (vii). The introduction of the further reaction (12) or (x*a*)

$$2HO_2 = 2OH + O_2 \qquad (12)(xa)$$

which effectively short-circuits reaction (x) and (vii) would make the observed rate of pyrolysis $2(k_{xa}+k_x)/k_x$ times that of (vii). Although, this introduces an error into the derived value of k_{vii}, it does not affect the conclusion that the rate of slow oxidation of hydrogen should be close to the experimentally observable rate of pyrolysis of the hydrogen peroxide present. Thus the addition of (x*a*) to Baldwin's scheme does not affect the conclusions regarding the rate of the slow reaction. This is not true for the second explosion limit. Neglecting quadratic branching the second explosion limit results from the introduction of the branching reactions

$$H + O_2 = OH + O \qquad (ii)$$

$$O + H_2 = OH + H \qquad (iii)$$

and explosion occurs when (iv) just fails to balance (ii) and (iii). The limit pressure is $[M] = 2k_{ii}/k_{iv}$ and the explosion develops with extreme rapidity with an isothermal time constant $t = 1/k_{ii}[O_2]$ [48] which at 500° would be about 3×10^{-5} sec. Under these conditions the lifetime of H_2O_2 is several seconds and reaction (x) is a chain terminating reaction. In KCl-coated vessels chain termination occurs by removal of HO_2 at the walls of the reaction vessel before they react mutually by (x). Thus, in either case, at the second limit all HO_2 radicals are effectively " dead ". This interpretation is confirmed by the observation that when quadratic branching is allowed for, the second limit in boric-acid-coated vessels is close to that in a KCl-coated vessel. If reaction (x*a*) is introduced the explosion limit in boric-acid vessels should be higher than in KCl-coated vessels by a factor of $(k_{xa}+k_x)/k_x$. In order to explain the hydrocarbon oxidation results the ratio would need to be at least three. The maximum value for the ratio according to Baldwin would be about 1·25.[49] Thus reaction (x*a*) is inadmissible as one might also argue from its endothermicity. Both difficulties can be circumvented if an unstable peroxide H_2O_4 is postulated and if reaction (x*a*) is written

$$2HO_2 = HOO—OOH \qquad (xa')$$

$$HOO—OOH = 2OH + O_2. \qquad (viia)$$

For (x*a'*) to be effectively chain terminating at the second explosion limit the peroxide H_2O_4 must have a lifetime of at least 10^{-4} sec at 500°. This would imply an activation energy for decomposition of about 30 kcal if the reaction were unimolecular. There is some evidence for the existence of a compound which may be H_2O_4 although its properties do not meet the above requirements. Nekrasov, Skorokhodov, Kobozev and co-workers,[50] have shown that identical products are obtained either by freezing the products of a silent discharge through water vapour at −196° or by reaction of H atoms with liquid ozone. The initial product appears to be the HO_2 radical but measurements of the e.s.r. spectrum of the solid product at −196° reveal a free radical concentration of only 0·4 %. Since up to 60 % reaction can occur in the ozone reaction the major component of the product is not a free radical. On warming the solid it melts at between −60 and −70° and then decomposes to equimolar quantities of H_2O_2 and O_2 between −55 and −40° giving out 35 kcal/mole of oxygen liberated. It is suggested that the reaction occurring is

$$H_2O_4 = H_2O_2 + O_2, \qquad \Delta H = -35 \text{ kcal.}$$

From thermochemical data [51] the heat of formation of H_2O_4 in solution must be about −12 kcal and its heat of dissociation to HO_2 about +6 kcal. The lifetime

of the superoxide at −70° should be ~1 sec. The observed lifetime of about 100 sec at −50° requires an activation energy for decomposition of 15 kcal if the reaction is unimolecular. There are clearly discrepancies between the experimental data from frozen peroxy radical condensates and the requirements of the theory of hydrocarbon oxidation.

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Slow Oxidation of Ethane and Ethylene in the Gas Phase

Part 2.—Analytical Features

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From detailed analysis of the initial stages of the oxidation of ethane, water, ethylene and formaldehyde are the only significant initial products at 362° and acetaldehyde is an additional initial product at 318°. Methanol, ethanol, ethylene oxide, carbon monoxide and carbon dioxide are secondary products. As oxygen has no effect on the relative yields of initial products they are produced by reactions of the same kinetics. Between 362 and 318° there is a profound change in the distribution of initial products. It is proposed that the equilibrium (1) is established

$$C_2H_5 + O_2 = C_2H_5OO \qquad (1)$$

and that ethylene is formed by direct H atom abstraction from ethyl while formaldehyde is formed from the ethyl peroxy radical.

The initial products from the oxidation of ethylene are ethylene oxide, formaldehyde and acetaldehyde. The secondary products are the same as from ethane. Various possible mechanisms re discussed for their formation. It is concluded that HO_2 is the main radical attacking ethylene. The end products of the oxidations are methane, ethane (from ethylene) and ethanol.

The detailed analytical results presented here substantiate the conclusions outlined in part 1 and point to certain other unexpected features of the oxidations. In particular, it seems that an equilibrium

$$C_2H_5 + O_2 \rightleftharpoons C_2H_5OO$$

is established and that ethylene is formed by hydrogen abstraction from ethyl by oxygen, whereas formaldehyde is produced via a four-membered ring transition state of low entropy from the ethyl peroxy radical.

TABLE 1.—INITIAL PRODUCTS FROM THE OXIDATION OF ETHANE AND ETHYLENE

	mixtures pressures of		initial product yields in mole/100 moles hydrocarbon consumed				
code [a]	hydrocarbon	oxygen	water	ethylene	formaldehyde	acetaldehyde	methanol [b]
2E31	222	74	80 ± 10	50 ± 10	60 ± 5	1·8 ± 0·2	60 ± 10
2E11	221	221	80 ± 5	55 ± 10	60 ± 5	4·5 ± 0·5	60 ± 10
4E11	221	221	90 ± 5	70 ± 5	17 ± 2	—	—
6E31	222	74	90 ± 5	90 ± 5	12 ± 1	<0·2	20 ± 5
6E11	221	221	90 ± 5	90 ± 5	12 ± 1	<0·2	30 ± 5
6E12	148	296	90 ± 5	90 ± 5	12 ± 1	<0·2	20 ± 5
8E11	221	221	95 ± 5	95 ± 5	11 ± 1	—	—
			water or carbon monoxide		formaldehyde	ethylene oxide	acetaldehyde
2A11	221	221	20		150 ± 10	17 ± 2	1·6 ± 0·1
6A11	221	221	20		170 ± 10	8 ± 1	0·8 ± 0·1
6A12	111	222	20		170 ± 10	8 ± 1	0·5 ± 0·1

(*a*) Mixture code; first figure refers to reaction temperature in tens of degrees above 300°C: 2 = 318°; 4 = 340°; 6 = 362°; 8 = 386°. Letter gives hydrocarbon: E = ethane; A = ethylene. Last two figures give [hydrocarbon]/[oxygen] ratio.

(*b*) The figures for methanol are the maximum proportional yields in the intermediate stages of the reaction. Methanol is not an initial product.

EXPERIMENTAL

The details of the apparatus and analytical procedure have been described.[1] Details of the temperatures and compositions of mixtures are given in table 1.

RESULTS

When more than one product can arise from a common free radical the relative kinetics of their formation can be obtained by studying the effect of reactant concentrations on the product ratios.[2] In particular, if products are formed in reactions

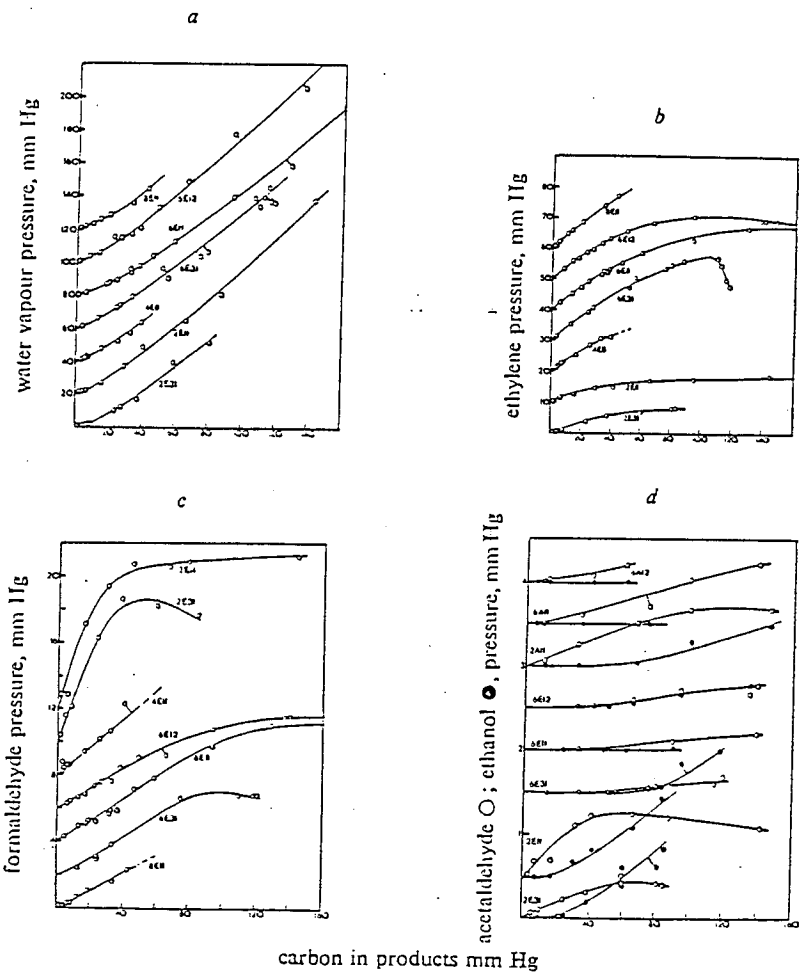


FIG. 1.—Development of products from the oxidation of ethane: (*a*) water, (*b*) ethylene, (*c*) formaldehyde, (*d*) acetaldehyde ○, ethanol ●. For convenience, most of the curves in this and later figures are displaced vertically. For mixture code, see table 1.

of identical kinetics their relative yields are unaffected by changes in reactant concentrations, and relative Arrhenius parameters can be obtained by measuring product ratios over a temperature range. It is essential to determine the product distribution in the early stages of the oxidation when secondary reactions are

minimal and to cover wide ranges of temperature and composition. Since the initial products from the oxidation of alkanes must arise from the reactions of alkyl radicals with oxygen, alkane concentration should have no effect on the initial product yields. We have accordingly investigated only the effect of oxygen pressure on the product yields.

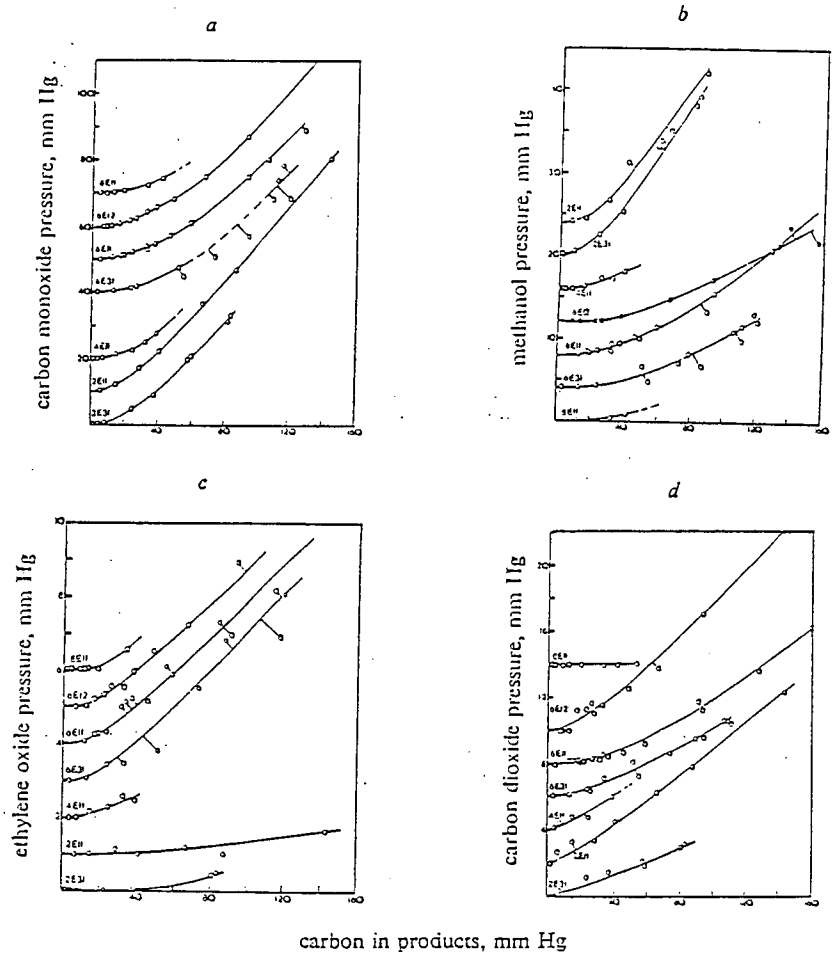


FIG. 2.—Development of products from the oxidation of ethane: (*a*) carbon monoxide, (*b*) methanol, (*c*) ethylene oxide, (*d*) carbon dioxide.

In order to distinguish between initial and secondary products we have plotted the yields of products against the total carbon content of the reaction products measured as a hypothetical C_1 gas pressure. The results for the initial and intermediate stages of the oxidation of ethane are presented in fig. 1*a*-1*d* and 2*a*-2*d*, and for the oxidation of ethylene in fig. 3*a*-3*d* and 4*a*, 4*b*. The figures for the ethylene containing mixtures include the data for the 1 : 1 ethane+oxygen mixture at 362° for comparison.

Water, ethylene and formaldehyde (fig. 1*a*, *b* and *c*) are the initial products from the oxidation of ethane between 318 and 386°. Acetaldehyde (fig. 1*d*) is a minor initial product at 318° and probably a trace initial product at the higher temperatures.

Carbon monoxide, methanol, ethanol and ethylene oxide (fig. 2*a*, 2*b*, 1*d* and 2*c*) are secondary products. Carbon dioxide is a minor product and at the lowest temperature may be an initial product formed in surface reactions (fig. 2*d*). At the higher temperatures it is a secondary product.

In the oxidation of ethylene at 318 and 362° formaldehyde and ethylene oxide are the main initial products (fig. 3*a* and 3*b*). Acetaldehyde is a minor initial product

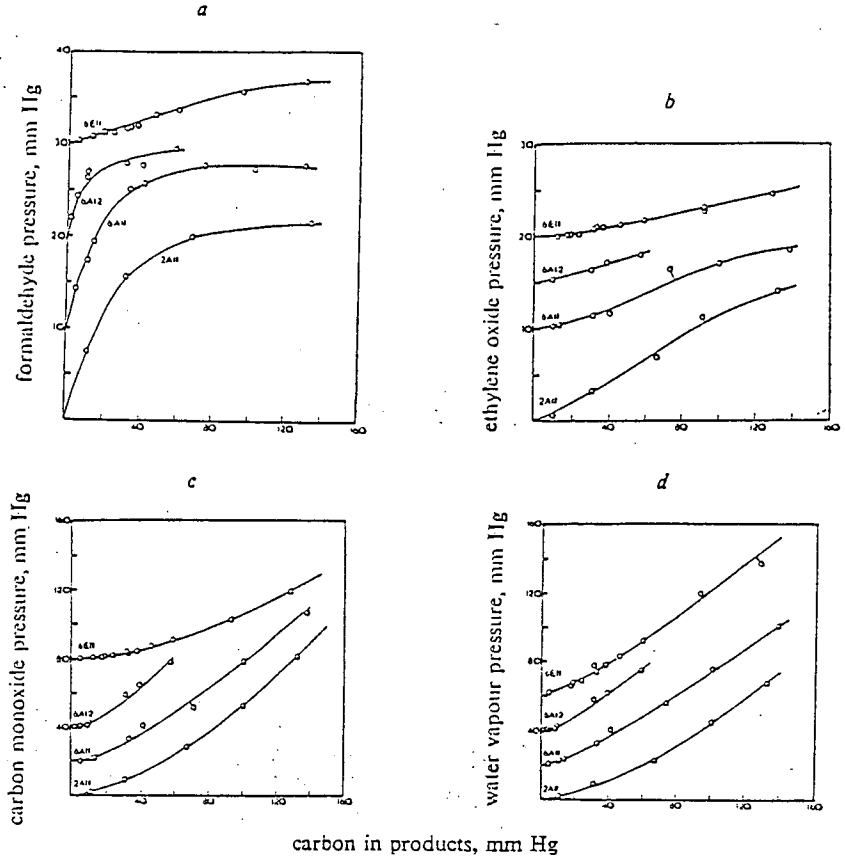


FIG. 3.—Development of products from oxidation of ethylene: (*a*) formaldehyde, (*b*) ethylene oxide, (*c*) carbon monoxide, (*d*) water.

(fig. 1*d*). The yield curves for water and carbon monoxide (fig. 3*c* and 3*d*) almost coincide and both rise sharply convex to the *X*-axis. It is therefore difficult to establish the initial gradients but it is likely that neither are initial products. They are probably formed by the oxidation of formaldehyde

$$CH_2O + \tfrac{1}{2}O_2 = CO + H_2O. \qquad (2)$$

Methanol, carbon dioxide and ethanol (fig. 4*a*, 4*b* and 1*d*) are secondary products.

The initial fractional yields derived by measurement of the initial gradients of the lines in fig. 1–4 are given in table 1. The key features of the results are:

(i) The yields of ethylene and formaldehyde produced from ethane rise to maximum values and eventually decline; the yield of formaldehyde in the oxidation of ethylene passes through a maximum. Thus formaldehyde and ethylene are

intermediate products in the oxidation of ethane between 318 and 386° and formaldehyde is an intermediate in the oxidation of ethylene.

(ii) There is no dependence of the initial yields of ethylene and formaldehyde from ethane on the oxygen pressure at either 318 or 362°.

(iii) There is a profound change in the distribution of products in the ethane oxidation as the temperature falls from 362 to 318°. The yields of formaldehyde

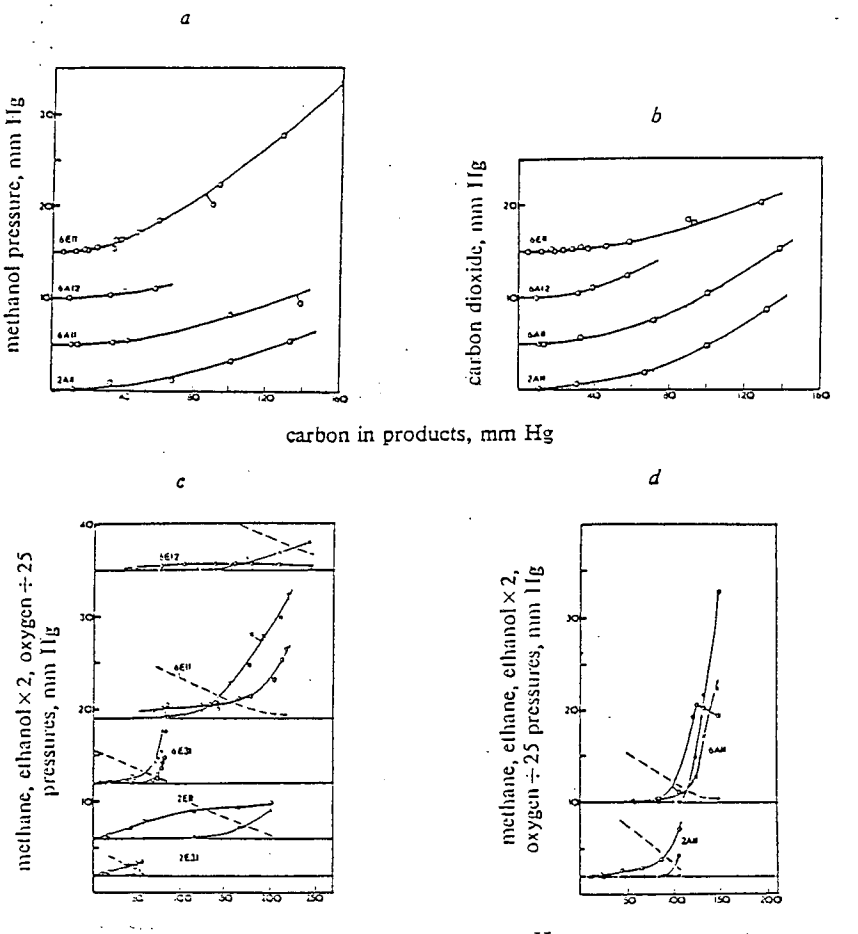
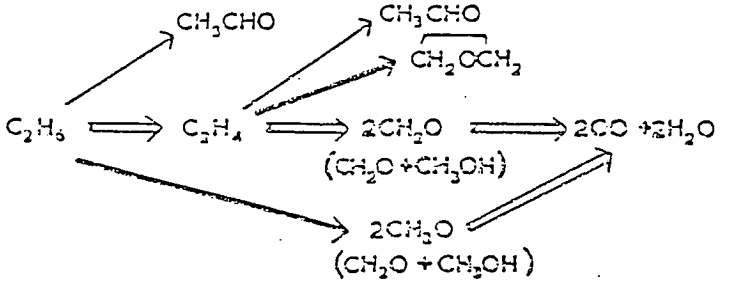


FIG. 4.—Development of products (*a*) methanol from ethylene, (*b*) carbon dioxide from ethylene, (*c*) end-products from ethane, (*d*) end-products from ethylene.

× methane; ○ ethanol; ● ethane; - - - oxygen

and acetaldehyde increase greatly between 362 and 318° while the yield of ethylene falls. In the intermediate stages of the oxidation the yield of methanol shows similar features and its formation may be linked with that of formaldehyde. In the oxidation of ethylene a similar but lesser effect is noted in the yields of ethylene oxide and acetaldehyde relative to formaldehyde. The activation energy differences associated with these changes in product distribution are about 35 kcal for the ethane oxidation and about 10 kcal for the ethylene oxidation.

These observations suggest that the main molecular stages in the ethane oxidation can be represented by the scheme below: the thickness of any line indicates qualitatively the fraction of the reaction proceeding by that path; the products written inside brackets are alternatives formed in the intermediate stages of the oxidation:



Minor features of the yield curves bear out this scheme. The yield of methanol in the intermediate stages of the oxidation follows the yield of formaldehyde in the initial stages when the temperature is altered. The yield curves for formaldehyde at the higher temperatures start with a positive gradient indicating that formaldehyde is an initial product and then the gradients of the curves increase slightly before they flatten off. This is due to an increase in the rate of formaldehyde production from the oxidation of ethylene. When the yields of ethylene and formaldehyde are constant the major reaction is effectively a straight-through run from ethane to carbon monoxide. The yield curves show that 70 % of the carbon consumed appears as CO and 70 % of the hydrogen as water.

The development of the products in the final stages of the oxidations are shown in fig. 4*c* and 4*d* for the ethane and ethylene oxidations respectively. In the oxidation of ethane at 362° methane and ethanol appear in the final stages. They arise only when the oxygen concentration is low but there is no simple relationship between the pressures of methane, ethanol and oxygen, and quantitative interpretation is not possible. At 318° ethanol, although not an initial reaction product, appears like methanol in the intermediate stages and there is no upward trend of the yield curve at the end of the oxidation as might have been expected by comparison with the curves for 362°. There therefore appear to be two mechanisms forming ethanol, one for the intermediate stages which increases in importance as the temperature falls and one for the final stages which decreases in importance as the temperature falls. Since the yield of methane falls as the temperature falls there may be a connection, between the reactions forming the two products in the final stages of the reaction.[1]

In the last stages of the oxidation of ethylene, ethane appears in addition to methane and ethanol. The yields of all three final products rise with rise of temperature. The formation of ethane in the ethylene oxidation suggests that the main reaction proposed for the oxidation of ethyl can be reversed:

$$C_2H_4 + HO_2 = C_2H_5 + O_2. \qquad (3)$$

DISCUSSION

ETHANE

The absence of dependence of the initial formaldehyde/ethylene ratio on oxygen pressure (varied four-fold at 362° and three-fold at 318°) indicates that both products are formed by reactions with the same dependence on oxygen concentration. Since

ethylene can hardly be formed other than by reaction (4),

$$C_2H_5 + O_2 = C_2H_4 + HO_2, \quad (4)$$

formaldehyde must be formed in a reaction which for kinetic purposes can be written

$$C_2H_5 + O_2 = CH_2O + CH_3O, \quad (5)$$

followed by the oxidation of methoxy since methanol is not an initial product of the reaction

$$CH_3O + O_2 = CH_2O + HO_2. \quad (6)$$

Evidence for reaction (6) is that the yield of methanol formed in the pyrolysis of dimethyl peroxide is greatly reduced by the addition of oxygen at about 200°C.[3] It may also occur in the oxidation of methanol [4] although here the predominant radical is probably CH_2OH not CH_3O. The formation of methanol later in the reaction must then be dependent upon the formation of a good hydrogen donor. Even at room temperature,[5] methanol can arise by reaction(7).

$$CH_3O + CH_2O = CH_3OH + CHO. \quad (7)$$

Since formaldehyde is certainly formed and consumed in the intermediate stages of the ethane oxidation this reaction is the most likely source of methanol. The analogous reaction (8) may also occur,

$$CH_2OH + CH_2O = CH_3OH + CHO, \quad (8)$$

but, being less exothermic [6] than (7), oxidation is the more likely fate of hydroxymethyl. These views on the formation of methanol agree with those of Fisher and Tipper [7] on the role of formaldehyde as a hydrogen donor in the oxidation of methane. The increase in the yield of methanol in the ethane oxidation as the temperature falls agrees with this set of reactions. The fraction of ethyl radicals giving rise to methoxy by reaction (5) rises as the temperature falls and so does the concentration of formaldehyde in the intermediate stages of the reaction: thus the rate of (7) should increase so as to give a higher proportional yield of methanol.

Acetaldehyde is only a trace product at the higher temperatures but is readily detectable as an initial product at 318°. It is the only initial product whose fractional yield depends upon the oxygen pressure to any extent, the initial yield being roughly proportional to the oxygen pressure. The formation of acetaldehyde by a reaction of higher order in oxygen than formaldehyde requires a reaction scheme such as

$$C_2H_5 + O_2 = C_2H_5OO \quad (1)$$

$$C_2H_5OO = CH_2O + CH_3O \quad (9)$$

$$C_2H_5OO + O_2 = CH_3CHO + OH + O_2. \quad (10)$$

Reaction (9) requires a four-membered ring transition state of low entropy but the direct decomposition of C_2H_5OO to give acetaldehyde and hydroxyl proposed by Norrish [8] necessitates an even more unlikely transition state. Therefore, the formation of acetaldehyde from the ethyl peroxy radical may conceivably only occur by the formation of a 6-membered ring which includes a second oxygen molecule.

Ethanol is not an initial product of the reaction but it is formed in approximately the same yield as acetaldehyde and so might be an alternative product to acetaldehyde formed by a mechanism similar to that proposed for methanol. However, the yield of acetaldehyde depends upon the oxygen concentration while that of ethanol does not. Thus, ethanol cannot be regarded as a substitute product for acetaldehyde. It probably arises from the addition of OH to ethylene followed by abstraction by the CH_2CH_2OH radical:

$$CH_2CH_2 + OH = CH_2CH_2OH \quad (11)$$

$$CH_2CH_2OH + CH_2O = CH_3CH_2OH + CH_2O, \quad (12)$$

which cannot otherwise be oxidized or decompose. The low yield of ethanol in the intermediate stages of the reaction is then in accord with the view that the OH concentration is much lower than the HO_2 concentration. Ethylene oxide is not an initial product from ethane and therefore reaction (13)

$$C_2H_5OO = \overline{CH_2—O—CH_2} + OH \qquad (13)$$

does not occur.

The striking increase in the aldehyde/ethylene ratio as the temperature falls from 362 to 318° requires an apparent activation energy difference $E_4 - E_5 = 35$ kcal, and an exceptionally low A factor ratio A_5/A_4. A possible explanation is that the equilibrium (1) is established, and that whereas ethylene is formed by a direct abstraction by oxygen from ethyl, formaldehyde is eventually formed as a result of the decomposition of the peroxy radical by reaction (9). This scheme may be represented as

$$C_2H_4 - HO_2 \xleftarrow{(4)} C_2H_5 + O_2 \underset{(-1)}{\overset{(1)}{\rightleftharpoons}} C_2H_5OO \xrightarrow{(9)} CH_2O + CH_3O.$$

Provided that the equilibrium (1) is not disturbed by these two reactions, then the apparent activation energy difference and A factor ratio are

$$E_4 - E_5 = E_4 - \Delta H_1 - E_9; \quad A_4/A_5 = A_4 \exp\left[-\Delta S_1/R\right]/A_9.$$

The only well-established peroxy bond strength is that in HO_2, D(H—OO) = 45 kcal.[9] An upper limit may be set to D(R—OO) on the basis of the reactions of RO_2 radicals. Since the peroxy radicals CH_3OO,[5] C_2H_5OO [10] and C_4H_9OO [11] disproportionate at room temperature to give the appropriate alkoxy radicals, and since these reactions can hardly be endothermic, the maximum R—OO bond strengths can be evaluated from known thermochemical data on the alkyl and alkoxy radicals.[6] This calculation gives 30 kcal. A value of $\Delta H_1 = -25$ kcal is therefore reasonable. The discovery of substantial quantities of ethane in the end stages of the oxidation of ethylene indicates that, even in the presence of moderate concentrations of oxygen, ethyl radicals can abstract hydrogen atoms from suitable H donors in preference to being oxidized. The direct abstraction reaction (4) may therefore have an activation energy of up to 10 kcal. Reaction (9) is exothermic and although it passes through a transition state of low entropy it may still have a near-zero activation energy. Thus, an overall activation energy difference $E_4 - E_5$ of about 35 kcal is possible.

The C_2H_5OO radical is similar to the n-butane molecule; the translational and rotational entropies are similar, and only the entropy contribution from internal degrees of freedom, vibrations and internal rotations will be significantly different. Now the entropies of straight chain molecules may be divided into components for the vibrations and internal rotations of the chain,[12] and components for the vibrations and internal rotations of the C—H bonds and CH_3 groups. The entropies for the chain processes in the two molecules should be similar, but those due to the vibrations of the C—H bonds and the internal rotations of the CH_3 groups in the C_2H_5OO radical will be exactly half those in the n-butane molecule. Allowing for the change in symmetry number and electronic degeneracy, the entropy of the peroxy radical can thus be calculated. The entropy of the ethyl radical can be taken as close to that of ethane,[13] again with allowance made for change in symmetry number and electronic degeneracy. Calculating in this way the entropy loss in the formation of the C_2H_5OO radical from C_2H_5 and O_2 is about 32 cal/deg. mole between 300 and 700° at 1 atm.

The entropy loss on forming the transition state in reaction (9) may also be

estimated. Since the transition state will be a four-membered ring all free rotations and low frequency chain vibrations will be lost. There are two internal rotations (one for the chain and one for the CH_3 group) and three low frequency chain vibrations. The entropy loss will then be about 25 cal deg.$^{-1}$ mole^{-1} and A_9 will be approximately $10^{13} \exp[-25/1{\cdot}99] = 10^{7{\cdot}5}$. The A factor for reaction (4) will be close to the collision frequency or $\sim 10^{10}$ atm^{-1} sec^{-1}. The ratio of the rates of formation of ethylene and formaldehyde can therefore be estimated as

$$R_4/R_9 \equiv R_4/R_5 = \{A_{-1} \exp[-\Delta S_1/R]/A_9\} \exp[(-E_4+\Delta H_1+E_9)/RT] = 10^{9{\cdot}5} \exp[(-E_4+E_5)/RT].$$

Since the experimental ratio is about 3 at 600°K a maximum activation energy difference of about 25 kcal is obtained since larger entropy contributions in reactions (1) and (9) are unlikely. This compares with the experimental value of 35 kcal and shows that the unexpected temperature dependence of the aldehyde/ethylene yield is still not fully explained.

For equilibrium (1) to be insignificantly disturbed, reaction (9) must be considerably slower than (−1). If (−1) is ten times as fast as (9), then

$$10^{7{\cdot}5} = 0{\cdot}1\, A_{-1} \exp[-25000/1{\cdot}99 \times 600],$$

whence $A_{-1} = 10^{17{\cdot}5}$, an unacceptably high value. Dingledy and Calvert [10] have measured the rate of reaction (1) and obtained the value $k_1 = 10^{12{\cdot}6}$ cm^3 mole^{-1} sec^{-1} = 10^8 atm^{-1} sec^{-1}. If $\Delta S_1^\circ = 32$ cal deg.$^{-1}$ mole^{-1} we obtain $A_{-1} = 10^{15}$ sec^{-1}. The A factor for the decomposition of the ethyl peroxy radical is therefore likely to be high but not high enough to allow reaction (9) to be slower than (−1). If equilibrium between ethyl and ethyl peroxy is the correct explanation of the observed temperature dependence of the aldehyde/ethylene ratio then the entropy loss in reaction (9) must be larger than 25 cal deg.$^{-1}$ mole^{-1}. It is difficult to accept this.

The appearance of methane and ethanol at the close of the oxidations of ethane and ethylene is not explained by any simple mechanism. The ethyl radical cannot pyrolyze and the ethyl peroxy radical could only give rise to methyl and formic acid, by an extremely improbable reaction. Furthermore, the final yield of methane is so large that substantial quantities of formic acid should have been observed; and, in addition, the yield of methane declines with temperature whereas the yield of products typically derived from the peroxy radical apparently increase with fall in temperature. The most probable sources of methyl are then the CH_3CO and CH_3CH_2O radicals. The former would be produced by radical attack on acetaldehyde. Although acetaldehyde is attacked during the oxidations at 318°C the proportion of acetaldehyde formed is never sufficient to account for all the methane observed even at 318° where the aldehyde yield is highest. At 362° only a very small fraction of the methane could arise in this way. The most likely precursor is therefore CH_3CH_2O.

Ethanol, apart from methane, could arise from the abstraction reactions of three radicals, CH_3CHOH, CH_2CH_2OH or CH_3CH_2O. The first of these radicals oxidizes to acetaldehyde and HO_2 at temperatures above 270°.[14] At 362° the observed yield of acetaldehyde is always too small to account for the formation of ethanol as an alternative product. The CH_2CH_2OH radical, probably formed by addition of OH to ethylene, is a plausible precursor of ethanol as it can neither be oxidized nor pyrolyze without rearrangement. It appears to explain the formation of ethanol in the intermediate stages of the reaction but there seems no reason why this radical should be formed only at the end of the ethane and ethylene oxidations at 362°. Thus the ethoxy radical is the most likely precursor of ethanol

formed at the close of the oxidations. The ethoxy radical cannot be formed in a simple way from ethyl or ethyl peroxy. A conceivable mode of formation is via ethyl hydroperoxide which itself might be formed by reaction (14).

$$C_2H_5OO + CH_2O = C_2H_5OOH + CHO. \quad (14)$$

However, this being a typical product formed from ethyl peroxy rather than ethyl, the formation of ethanol at the end of the reaction would be encouraged by a reduction in temperature, which is not the case. Other possible sources of ethoxy are radical + radical reactions. Three possibilities are

$$2C_2H_5OO = 2C_2H_5O + O_2 \quad (15)$$

$$C_2H_5OO + HO_2 = C_2H_5O + O_2 + OH \quad (16)$$

$$C_2H_5 + HO_2 = C_2H_5O + OH. \quad (17)$$

The first two reactions would occur throughout the oxidation and the absence of ethanol in the intermediate stages of the oxidation at 362° is explained by assuming oxidation of the ethoxy radicals. Since there is no obvious alternative product in sufficient yield (acetaldehyde or ethylene oxide) only (17) is likely. The concentration of ethyl will rise as the reaction proceeds due to the reversal of the equilibrium (1) so the early formation of ethoxy and thence ethanol from this reaction is not expected. The effect of temperature is also explained: as the temperature is reduced the equilibrium (1) moves further to the right-hand side and the concentration of ethyl decreases as shown in table 2. In addition, the overall oxidation is slower and the radical concentrations lower. Thus, the rate of (17) is strongly temperature dependent. The formation of ethane at the end of the oxidation of ethylene follows from the increasing stability of the ethyl radical as the temperature is raised, particularly if reaction (4) requires a significant activation energy. In agreement, the yield of ethane increases from 318 to 362°.

TABLE 2.—EQUILIBRIUM CONSTANT FOR THE REACTION

$C_2H_5 + O_2 = C_2H_5OO$; $\Delta H = -25$ kcal mole^{-1}; $\Delta S^\circ = -32$ cal deg.$^{-1}$ mole^{-1}

temp. °K	500	600	650	700	750	800
$\log_{10} K_p =$ $(\Delta S^\circ - \Delta H/T)/4{\cdot}6$	−3·7	−2·2	−1·5	−0·9	+0·3	+0·3
[EtOO]/[Et]						
$[O_2] = 10$ mm Hg	100	2·0	0·4	0·10	0·025	0·007
$[O_2] = 100$ mm Hg	1000	20	4	1·0	0·25	0·07

ETHYLENE

There are several ways of explaining the formation of formaldehyde as the major product from the oxidation of ethylene above 320°C. The simplest [15] is the direct addition of an oxygen molecule across the double bond to give a four-membered ring peroxide which then decomposes (reactions (18) and (19)):

$$C_2H_4 + O_2 = \overline{CH_2—O—O—CH_2} \quad (18)$$

$$\overline{CH_2OOCH_2} = 2CH_2O. \quad (19)$$

These reactions explain the initial pressure decrease observed in this and other olefin oxidations if the ring peroxide has some stability. However, the oxidations of ethane and ethylene are closely interlinked and ethylene oxide is also an initial product of the ethylene oxidation; it is therefore extremely unlikely that the major

part of the oxidation of ethylene proceeds by a molecular rather than a free radical process. The direct addition of oxygen, if it occurs, must be a minor reaction. A more likely cause of the pressure decrease is a partial polymerization [15] which might occur by the series of free radical steps initiated by the addition of HO_2 to ethylene

$$C_2H_4 \xrightarrow{+HO_2} HOOC_2H_4 \xrightarrow{+O_2} HOOC_2H_4OO \xrightarrow{+C_2H_4} HOOC_2H_4OOC_2H_4 \xrightarrow{+RH}$$

$$HOO(C_2H_4OO)_nH \xrightarrow{\text{pyrolysis}} 2nCH_2O + H_2O_2.$$

Since the observed pressure decreases are small compared with the amount of oxidation at any stage, the reactions responsible must always be of minor importance and it is unlikely that this type of polymerization reaction is the main source of formaldehyde in the oxidation.

There are at least three plausible chain mechanisms which can explain the formation of formaldehyde although none of them explain the initial pressure decrease at low temperatures. The earliest mechanism,[16] based on analytical and kinetic evidence, was:

$$C_2H_4 + OH = C_2H_5O \quad (20)$$

$$C_2H_5O = CH_3 + CH_2O \quad (21)$$

$$CH_3 + O_2 = CH_2O + OH. \quad (22)$$

The radical formed in (20) would be expected to be CH_2CH_2OH and an isomerization to CH_3CH_2O would be required before reaction (21) could occur. This would require 20-30 kcal activation energy, and it might be argued that the formation of ethanol should be observed in the initial stages. A more serious objection to the scheme comes from the oxidation of higher olefins where the initial reaction can generally be represented by

$$R^aR^bC : CR^cR^d + O_2 = R^aR^bC : O + O : CR^cR^d. \quad (23)$$

If reactions (20)-(22) held generally then in the oxidation of 2-methyl-but-2-ene reaction (22) would produce either ethyl or isopropyl radicals. Above 320°, these radicals are oxidized predominantly to the olefins and therefore ethylene and propylene would be the major products. Likewise with but-2-ene, ethylene should be an important product at temperatures above 320° contrary to obererva tion.[17, 18] Skirrow *et al.* have overcome this disadvantage by proposing that the radical formed in (20) is further oxidized:

$$CH_2CH_2 + OH = CH_2CH_2OH \quad (20)$$

$$CH_2CH_2OH + O_2 = OOCH_2CH_2OH \quad (23)$$

$$OOCH_2CH_2OH = CH_2O + CH_3O + OH. \quad (24)$$

The formation of ethylene oxide can then be accommodated by incorporating reaction (25),

$$CH_2CH_2OH + O_2 = CH_2OCH_2 + HO_2. \quad (25)$$

This scheme has two disadvantages. Firstly, reaction (25) requires a strained low-entropy transition state and would not be expected to complete effectively with the addition of oxygen to CH_2CH_2OH. Secondly, in the oxidation of ethane the radical in the highest concentration is almost certainly HO_2 since any OH radicals even if they are mainly responsible for removing ethane will quickly be converted to HO_2 by reactions (26) and (4):

$$OH + C_2H_6 = H_2O + C_2H_5 \quad (26)$$

$$C_2H_5 + O_2 = C_2H_4 + HO_2. \quad (4)$$

Likewise in the oxidation of ethylene, after the initial stages, OH whenever formed will be rapidly converted to HO_2 via the reaction with formaldehyde. In both oxidations HO_2 is likely to be the predominant radical and since the additions of HO_2 and OH to ethylene will both be exothermic their activation energies are both likely to be small. Thus the major part of the attack on ethylene will be carried on by HO_2. Accordingly, we prefer a third mechanism for olefin oxidations, involving the reactions (27)-(30):

$$CH_2CH_2 + HO_2 = CH_2CH_2OOH \quad (27)$$

$$CH_2CH_2OOH = CH_2O + CH_2OH \quad (28)$$

$$CH_2OH + O_2 = CH_2O + HO_2. \quad (29)$$

Reaction (28) is analogous to the decomposition of the ethyl peroxy radical into CH_3O and CH_2O and involves a four-membered ring transition state. The formation of ethylene oxide can occur by the direct reaction of HO_2 with ethylene

$$C_2H_4 + HO_2 = \overbrace{CH_2OCH_2} + OH. \quad (30)$$

This scheme has the advantage of accounting for the formation of small amounts of methanol in the ethylene oxidation. The CH_2OH radical formed in (38) has a lower heat of formation than CH_3O [6] and therefore abstracts with greater difficulty. Even in the presence of formaldehyde in high concentration, there is a high probability that it will be oxidized.

The fact that the yield of ethylene oxide increases as the temperature falls indicates that reaction (27) has a higher activation energy than (30). While reaction (30) involves a ring transition state, it is highly exothermic and may have a near-zero activation energy while reaction (27) might be expected to have a small positive activation energy.

There is probably a further way in which HO_2 can add to ethylene which accounts for the formation of ethane in the last stages of the ethylene oxidation

$$CH_2CH_2 + HO_2 = CH_3CH_2 + O_2. \quad (-4)$$

This reaction must occur throughout the oxidation but normally the ethyl radicals are oxidized back to ethylene. However, a small proportion will give rise to formaldehyde and methanol and this may be the source of the methanol in the ethylene oxidation rather than abstraction by CH_2OH.

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THE FLASH PHOTOLYTIC REDUCTION OF 2-ACETONAPHTHONE IN SOLUTION

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THE FLASH PHOTOLYTIC REDUCTION OF 2-ACETONAPHTHONE IN SOLUTION

W. A. BRYCE AND C. H. J. WELLS

INTRODUCTION

The excited intermediate responsible for the photolytic reduction of aromatic ketones is believed to be the triplet state (1, 2). The initial stages of the mechanism can be represented by the following sequence of reactions:

$$R_2CO + h\gamma \rightarrow R_2CO_S^* \quad [1]$$

$$R_2CO_S^* \rightarrow R_2CO \quad [2]$$

$$R_2CO_S^* \rightarrow R_2CO_T^* \quad [3]$$

$$R_2CO_T^* \rightarrow R_2CO \quad [4]$$

$$R_2CO_T^* + DH \rightarrow R_2COH + D\cdot \quad [5]$$

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The ketone molecule is excited initially to an upper singlet state which will decay back to the ground state or form a triplet state by internal conversion. The triplet state will either decay to the ground state or abstract a hydrogen atom from the solvent DH to form a ketyl radical, $R_2\dot{C}OH$. The ketyl radical forms the final products by reacting with the solvent, DH, with the radical, $\dot{D}$, or by dimerization.

Since the photolysis of an aromatic ketone can result in the formation of both the triplet state of the ketone and the ketyl radical as intermediates care must be exercised in the assignment of transient absorption spectra. McClure and Hanst (3) observed the triplet absorption in the flash photolysis of benzophenone in a rigid medium. The close similarity between this absorption and the transient absorption in solution originally led Porter and Windsor (4) to believe that the transient observed in solution was also the triplet state. The absorption was subsequently assigned (5) to the relatively long-lived ketyl radical $C_6H_5\dot{C}OHC_6H_5$. The triplet absorption was not observed in solution, presumably because of the rapidity of the hydrogen transfer occurring in reaction [5].

It has been reported (6) that certain naphthoyl ketones, including 2-acetonaphthone, are not photoreduced in the presence of a weak hydrogen donor such as a secondary alcohol. The reduction of 2-acetonaphthone does occur, however, if a more active hydrogen donor, such as tributylstannane, is added to the system (7). This suggests that the corresponding ketyl radical for 2-acetonaphthone can only be formed in the presence of active hydrogen donors, and that any transient absorption observed when 2-acetonaphthone is photolyzed in the presence of a weak donor must be that of the triplet state. The present work was undertaken to study the decay of the triplet absorption of 2-acetonaphthone in an 'inert' solvent and to characterize any transient absorption that may be observed when 2-acetonaphthone is photolyzed in the presence of tributylstannane. The effect of the addition of 1-naphthol and triphenylene as quenching or energy-transfer agents in the system was also studied.

EXPERIMENTAL

2-Acetonaphthone (Eastman Kodak White label) was recrystallized three times from petroleum ether (60–80°). 1-Naphthol (Eastman Kodak White label) was vacuum sublimed, recrystallized three times from spectroscopic grade benzene, and resublimed. Triphenylene (Aldrich Chemical Corp.) was zone refined. Tributylstannane was prepared from tributyltin chloride (Metal and Thermit Corp.) by the method of Van der Kerk and Luitjen (8). The solutions were all made up in spectroscopic grade benzene (Eastman Kodak) and were thoroughly degassed before flashing. This was done by a freeze–pump–melt–freeze–pump procedure combined with trap-to-trap distillation under high vacuum.

The flash apparatus was of conventional design, the photolysis lamp consisting of a quartz tube of 42-cm length and 3.8-cm O.D., araldited into cylindrical stainless steel electrodes of a design developed by Claesson and Lindqvist (9). Discharge occurred between 1/4-in. tungsten rods mounted in the centers of the electrodes. The lamp was mounted coaxially in a cylindrical brass can coated on the inside with magnesium oxide, and was generally filled with nitrogen to a pressure of 5 cm. The duration of the flash on discharging a 66 μf condenser bank through the lamp at 10 kv was approximately 12 microseconds. The spectroscopic lamp was similar in design to the photolysis lamp but with a quartz capillary of 3-cm length and 2-mm bore. It was filled with nitrogen to a pressure of 4 mm and had a flash-time of 5 microseconds for a 50 joule flash. The timing of the spectroscopic flash was controlled by an electronic delay unit and checked by means of an oscilloscope. The discharge was focused through the reaction vessel onto the slit of a Hilger-Watts E 742 Automatic quartz spectrograph.

The reaction vessel was a quartz tube 21 cm long and 15 mm in diameter located beside the photolysis lamp. It was surrounded by a double quartz cylindrical vessel with an annular space 6 mm wide which could be filled with filter solutions. The absorption spectra were photographed on either Kodak 103-F or Ilford HP3 plates. The plates were scanned with a Hilger-Watts recording microdensitometer and the deflection readings at each wavelength converted to optical density of transient from a previously constructed calibration graph. Each plate was calibrated by inserting alumina-on-quartz neutral density filters between the reaction vessel and the spectrograph, firing the photolamp and the spectroscopic lamp with the delay set at 14 microseconds, and measuring the corresponding plate density.

RESULTS AND DISCUSSION

The transient absorption observed when a 1.01×10^{-3} M solution of 2-acetonaphthone in benzene was flashed is given by curve A in Fig. 1. The concentration of 2-aceto-

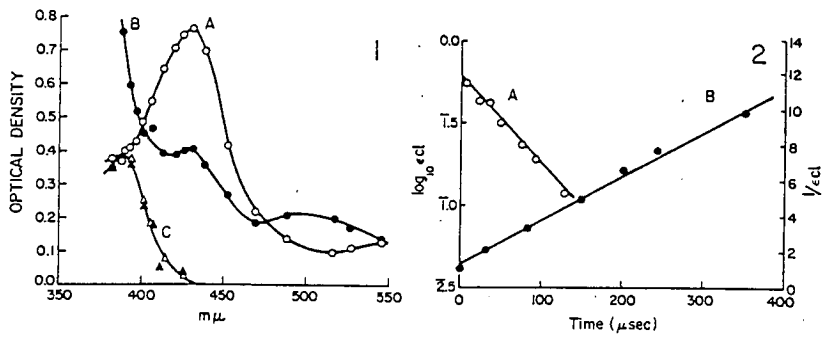

FIG. 1. Transient absorption spectra following photolysis in benzene solution of (A) 1.01×10^{-3} M 2-acetonaphthone; (B) 1.01×10^{-3} M 2-acetonaphthone + 0.17 M tributylstannane; (C) ▲, 0.90×10^{-4} M 1-naphthol, no filter present; △, 1.01×10^{-3} M 2-acetonaphthone + 0.90×10^{-4} M 1-naphthol; filter solution, 0.5 M 1-naphthol. Flash energy, 2220 joules; delay, 11 microseconds.

FIG. 2. (A) Logarithm of the optical density of the triplet state of a 1.01×10^{-4} M solution of 2-acetonaphthone in benzene, against time. (B) Reciprocal of the optical density of the triplet state of a 0.90×10^{-2} M solution of 2-acetonaphthone in benzene, against time. Flash energy, 2220 joules.

naphthone and the absorption spectrum of the solution were unchanged after 30 flashes at 2220 joules per flash, showing that the transient absorption was that of the triplet state. When a solution 1.01×10^{-3} M in 2-acetonaphthone and 0.17 M in tributylstannane was flashed under the same conditions a transient absorption was obtained (curve B, Fig. 1) which differed from that of the triplet state. The peak maximum of this absorption band lies below 385 mμ, and is hidden by the singlet–singlet absorption band of 2-acetonapthone. The new absorption band had a relatively long lifetime as compared to the triplet absorption band and could be detected some 10 milliseconds after flashing. This long lifetime, plus the observation that 20% of the 2-acetonaphthone had been decomposed after 20 flashes, indicates that the transient absorption spectrum was that of the ketyl radical $C_{10}H_7\dot{C}OHCH_3$. The maximum in the absorption in curve B at 430 mμ may be caused by simultaneous triplet–triplet absorption of 2-acetonaphthone, and hence it was not possible to decide whether the spectrum in this region is due to the ketyl radical only, or to a combination of triplet and ketyl radical absorption.

The kinetics of the decay of the triplet state was investigated for different initial concentrations of 2-acetonaphthone. For a 1.01×10^{-4} M solution a plot of the logarithm of the optical density against time was linear within the limitations of plate photometry (Fig. 2, curve A). The first-order rate constant, k_1, had a value of $1.27\pm0.25\times10^4$ sec^{-1}, and thus the triplet-state lifetime was $0.75\pm0.25\times10^{-4}$ sec. When the concentration of 2-acetonaphthone was increased to 0.90×10^{-2} M, the decay was second order (Fig. 2, curve B) with a rate constant k_2 of $5.5\pm0.9\times10^5$ $(\epsilon C)^{-1}$ sec^{-1}, where ϵ is the molar extinction coefficient and C is the molar concentration. The transition from primarily first-order kinetics at low concentrations to second-order kinetics at the higher concentrations suggests that at the lower concentrations there will be some contribution to the decay from second-order quenching, and hence the value obtained for the rate constant, k_1, is a maximum.

It has been shown (10, 11) that selective excitation of the triplet level of one molecule in the presence of another molecule with a lower-lying triplet level can lead to energy transfer from the upper triplet to the lower triplet. It was therefore of interest to see if the triplet state of 2-acetonaphthone could be quenched by the addition to the solution of a molecule with a lower-lying triplet level, and to examine the consequent effect on the extent of photoreduction. As illustrated schematically in Fig. 3, the energy levels of 1-naphthol relative to those of 2-acetonaphthone made it suitable for use as a quencher.

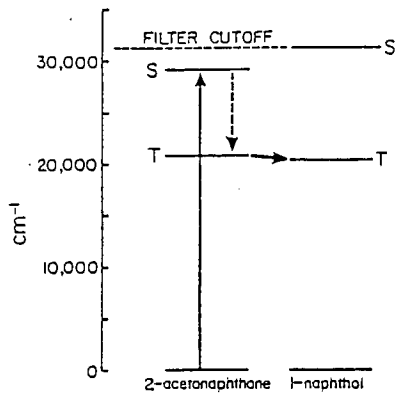

FIG. 3. Energy level diagram of the first excited states of 2-acetonaphthone and 1-naphthol.

Selective excitation of the 2-acetonaphthone in the presence of 1-naphthol was achieved by surrounding the solution to be flashed with a concentrated solution of 1-naphthol. The transfer of energy between the 2-acetonaphthone triplet and the 1-naphthol triplet is shown by the results presented in Fig. 1. Curve A illustrates the triplet-state absorption for a 1.01×10^{-3} M 2-acetonaphthone solution. Curve C shows the triplet absorption of a 0.90×10^{-4} M 1-naphthol solution with no filter in the system, and also shows the transient absorption of a solution which is 0.90×10^{-4} M in 1-naphthol and 1.01×10^{-3} M in 2-acetonaphthone with the 1-naphthol filter present. When a 0.90×10^{-4} M solution of 1-naphthol was flashed with the filter solution present no transient absorption could be detected.

Transfer of energy from the first excited singlet of 2-acetonaphthone to the corresponding state in 1-naphthol is unlikely since this state is higher in 1-naphthol than in 2-acetonaphthone. Direct transfer from the first excited singlet state of 2-acetonaphthone to the triplet of 1-naphthol is also unlikely as this is a spin-forbidden process and, for many donor–acceptor pairs, has been shown to be unimportant compared with triplet–triplet energy transfer (10–12).

The quenching effect of 1-naphthol on the photoreduction of 2-acetonaphthone is shown by the results given in Fig. 4(*a*). Solutions which were 1.01×10^{-3} M in 2-acetonaphthone and 0.42 M in tributylstannane were flashed in the presence of various amounts of 1-naphthol. The results show that the decomposition of the 2-acetonaphthone decreased as the concentration of 1-naphthol increased. The observation that 1-naphthol removes triplet excitation energy from 2-acetonaphthone and also quenches the photoreduction provides convincing evidence that the triplet state is the active intermediate in the photoreduction.

The possibility that 1-naphthol reacted with the tributylstannane on flashing, or that a complex was formed between the 1-naphthol and 2-acetonaphthone was ruled out by the

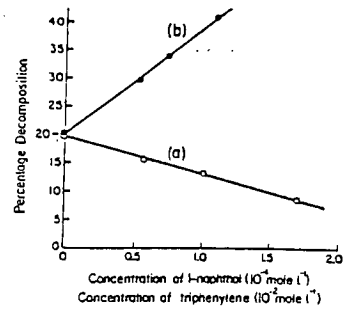

FIG. 4. Percentage decomposition of 2-acetonaphthone against concentration of 1-naphthol and triphenylene in benzene solution: (*a*) 1.01×10^{-3} *M* 2-acetonaphthone + 0.42 *M* tributylstannane + 1-naphthol; filter solution, 0.5 *M* 1-naphthol. (*b*) 5.2×10^{-4} *M* 2-acetonaphthone + 0.21 *M* tributylstannane + triphenylene; no filter present. Flash energy, 2220 joules; number of flashes, 20.

observation that the absorption spectrum of a solution containing 1-naphthol and tributylstannane was the same before and after being flashed, and by the fact that the absorption spectrum of a solution of 2-acetonaphthone and 1-naphthol after flashing was identical with the combined spectra of the two solutes in separate solutions.

Since the action of 1-naphthol as a quencher was to remove triplet-state energy it follows that a molecule which could transfer energy to the 2-acetonaphthone triplet should sensitize the photoreduction. The requirements for an ideal sensitizer are: (1) a first triplet level lying above that of 2-acetonaphthone; (2) a first excited singlet lying below that of 2-acetonaphthone; and (3) a triplet–triplet absorption band lying in a region of the spectrum different from that for 2-acetonaphthone to enable the energy transfer between triplets to be followed by plate photometry. Unfortunately it was not possible to obtain a molecule with all three requirements. Triphenylene, however, does meet the first requirement and was used as a sensitizer. The results presented in Fig. 4(*b*) show that the addition of triphenylene to a solution of 2-acetonaphthone and tributylstannane greatly increases the rate of removal of 2-acetonaphthone from the system. The absorption spectra of triphenylene and 2-acetonaphthone are so similar that it was not possible selectively to excite the triphenylene. However the concentration of 2-acetonaphthone was 5.2×10^{-4} *M* while the lowest concentration of triphenylene used was 5.0×10^{-3} *M* so that it is safe to assume that most of the light was absorbed by the triphenylene. Owing to the closeness of the energies of the first excited singlet states of 2-acetonaphthone and triphenylene it was not possible to decide whether the 2-acetonaphthone was excited to its triplet state by direct energy transfer from the triphenylene triplet or by singlet–singlet energy transfer between the two molecules followed by internal conversion of the singlet of 2-acetonaphthone to the triplet state.

Experiments similar to those carried out with 1-naphthol gave no indication that triphenylene and 2-acetonaphthone formed a complex in solution, or that triphenylene reacted with tributylstannane on flashing.

ACKNOWLEDGMENTS

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COMPLEXES OF DICHLOROMALEIC ANHYDRIDE WITH SOME METHYLBENZENES AND THE ELECTRON AFFINITIES OF MALEIC ANHYDRIDE AND DICHLOROMALEIC ANHYDRIDE

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Abstract—Isomeric 1:1 complexes and higher order complexes are formed between dichloromaleic anhydride and either durene, pentamethylbenzene or hexamethylbenzene in carbon tetrachloride solution. The electron affinities of dichloromaleic anhydride and maleic anhydride as calculated from the charge transfer transition energies of the corresponding complexes are 0·5$_3$ and 0·1$_1$ ev respectively.

ACCEPTOR properties of anhydrides are well established from studies of their charge transfer complexes with aromatic hydrocarbons.[1] The association constants and the molar absorptivities of the complexes have been computed by means of the Benesi-Hildebrand equation or one of its many variations.[2] However Johnson and Bowen[3] have recently shown that association constants derived by means of the Benesi-Hildebrand equation are only meaningful if the value of the association constant is independent of the wavelength of measurement. In view of this and the fact that there are no reports on the electron acceptor properties of dichloromaleic anhydride, the charge transfer interaction between dichloromaleic anhydride and some methylbenzenes has been investigated and the variation of the association constant with wavelength reported.

The absorption spectra of mixtures of dichloromaleic anhydride with durene, pentamethylbenzene and hexamethylbenzene in carbon tetrachloride gave broad featureless bands in the region 355–430 mμ which were not observable in the spectra of the individual components. These bands were ascribed to the formation of a charge transfer complex or complexes since good straight line plots were obtained for the Benesi-Hildebrand relation:

$$\frac{1}{D} = \frac{1}{K\varepsilon a} \cdot \frac{1}{b} + \frac{1}{\varepsilon a} \qquad (1)$$

where a is the constant acceptor concentration, b the varied donor concentration ($b \gg a$), ε the molar absorbance of the complex, D the optical density for a 1 cm light path and K (l. mole^{-1} units) is the association constant for complex formation.

The positions of the band maxima, the values of the association constants and molar absorptivities (calculated for λ_{max}) at 20·2 and 40·1° are given in Table 1, while

[1] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.* 75, 3776 (1953); W. G. Barb, *Trans. Faraday Soc.* 49, 143 (1953); M. Chowdhury and S. Basu, *Ibid.* 56, 335 (1960); L. L. Ferstandig, W. G. Toland and C. D. Heaton, *J. Amer. Chem. Soc.* 83, 1151 (1961).

[2] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.* 71, 2703 (1949); R. L. Scott, *Rec. Trav. Chim.* 75, 787 (1956); N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.* 81, 6138 (1959).

[3] G. D. Johnson and R. E. Bowen, *J. Amer. Chem. Soc.* 87, 1655 (1965).

the corresponding values at 20·2° over the wavelength range 355–430 mμ are given in Table 2.

Although the association constants are reasonably invariant in the region of the band maxima the values increase in each case at longer wavelengths. Jurinski,[4] Hayman[5] and Johnson and Bowen[3] have shown that this would be expected for the case where higher order complexes are formed simultaneously with 1:1 species. It is

TABLE 1. ASSOCIATION CONSTANTS (K) AND MOLAR ABSORPTIVITIES (ε) FOR COMPLEXES OF DICHLOROMALEIC ANHYDRIDE WITH METHYLBENZENES IN CARBON TETRACHLORIDE AT λ_{max} OF CHARGE TRANSFER ABSORPTION

Donor	λ_{max} mμ	K(l. mole^{-1}) 20·2°	40·1°	ε 20·2°	40·1°
Durene	360	1·08	0·67	1792	894
Pentamethylbenzene	372	2·40	1·67	2029	1670
Hexamethylbenzene	390	4·64	2·60	2042	1816

TABLE 2. ASSOCIATION CONSTANTS[a] (in l. mole^{-1}) AT 20·2° FOR DICHLOROMALEIC ANHYDRIDE–METHYLBENZINE COMPLEXES FOR ALL WAVELENGTHS STUDIED (NUMBERS IN PARENTHESIS ARE 95% PROBABILITY LIMITS)

mμ	Durene	PMB[b]	HMB[c]
355	1·10(0·10)	2·08(0·09)	4·98(0·16)
360	1·08(0·15)	2·35(0·11)	4·53(0·15)
365	1·12(0·12)	2·44(0·13)	4·01(0·22)
370	1·19(0·12)	2·32(0·19)	4·46(0·19)
372	—	2·40(0·20)	—
375	1·09(0·09)	2·40(0·26)	4·40(0·15)
380	1·11(0·15)	2·32(0·13)	4·58(0·12)
385	1·09(0·10)	2·35(0·14)	4·68(0·20)
390	1·00(0·13)	2·38(0·09)	4·64(0·10)
395	0·98(0·12)	2·46(0·12)	4·69(0·20)
400	1·49(0·21)	2·58(0·18)	4·70(0·16)
405	1·50(0·09)	2·55(0·21)	5·20(0·25)
410	1·62(0·14)	2·58(0·17)	5·41(0·21)
415	1·69(0·20)	2·67(0·18)	5·53(0·18)
420	—	2·90(0·21)	5·77(0·10)
425	—	—	6·01(0·18)
430	—	—	6·01(0·28)

[a] The mean value of five determinations. [b] Pentamethylbenzene
[c] Hexamethylbenzene

thus apparent that higher order complexes and 1:1 complexes are present in the dichloromaleic anhydride–methylbenzene systems studied. Jurinski and de Maine[6] have also observed an increase in association constant with increasing wavelength in the case of aromatic hydrocarbon–aromatic nitro compound complexes and attributed this to the formation of higher order complexes.

[4] N. B. Jurinski, *J. Miss. Acad. Sci.* **10**, 74 (1964).
[5] H. J. G. Hayman, *J. Chem. Phys.* **37**, 2290 (1962).
[6] N. B. Jurinski and P.A.D. de Maine, *J. Amer. Chem. Soc.* **86**, 3217 (1964).

The decrease in the molar absorptivities of the complexes with increasing temperature (Table 1) can be explained by the presence of "isomeric" or orientational complexes. The molar absorptivities of the complexes decreased with temperature over the complete range of the complex absorption band and comparison of the plots (not shown) of the molar absorptivity against wavelength at 20·2 and 40·1° did not reveal any significant change in the position of the band maxima or shape of the absorption band with increased temperature. Thus it would appear that the most stable species and hence the relatively more abundant at a higher temperature does not absorb at a different energy from any other complex.

The molar absorptivities of the complexes increase slightly with increasing complex stability (Table 1). As the electron donor becomes more effective and the association constant increases the transition moment increases and an increase in the molar absorptivity is observed. The contribution of contact charge transfer absorption to the total absorption intensity must be small, if any, as this would be reflected by a decrease in the absorptivity of the complex with increasing stability.[7]

According to Mulliken's theory of intermolecular interaction between electron-acceptor and electron-donor molecules the energy $h\nu_{CT}$ of electron transfer from donor to acceptor is related to the ionization potential I of the donor and the electron affinity EA of the acceptor by the expression:[8]

$$h\nu_{CT} = I - (EA - E) + \frac{c_1}{I - (EA - E)} \tag{2}$$

where E is mainly the energy of the coulomb attraction between D^+ and A^- after the transfer of one electron from the donor D to the acceptor A and c_1 is a constant. At sufficiently large ionization potentials ($I > 7{\cdot}5$ ev) the last term in the above expression may be neglected and the equation reduces to:

$$h\nu_{CT} = I - (EA - E) \tag{3}$$

For charge transfer complexes of the same bond type and configuration E may be considered constant, and for two acceptors of similar structure and one and the same donor the following relationship will apply:

$$(h\nu_{CT})_1 - (h\nu_{CT})_2 = EA_2 - EA_1 \tag{4}$$

The electron affinity of an acceptor 1 can be calculated from the charge transfer transition energies of complexes of acceptor 1 and acceptor 2 with the same donor if the electron affinity of acceptor 2 is known. The $h\nu_{CT}$ values for complexes of various aromatic hydrocarbons with *p*-chloranil, maleic anhydride and dichloromaleic anhydride in carbon tetrachloride are listed in Table 3 alongwith the values of the electron affinities of maleic anhydride and dichloromaleic anhydride calculated relative to the electron affinity of *p*-chloranil.

The mean values of the electron affinities of maleic anhydride and dichloromaleic anhydride are 0·11 and 0·53 ev respectively. Owing to the assumptions made in the derivation of Eq. 4 the accuracy in these values is probably not greater than about 0·1 ev. Briegleb[9] has previously calculated the electron affinity of maleic anhydride

[7] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.* 79, 4839 (1957).
[8] R. S. Mulliken, *J. Amer. Chem. Soc.* 72, 600 (1950); 74, 811 (1952); *J. Chem. Phys.* 19, 514 (1951).
[9] G. Briegleb, *Angew. Chem.* (Inter. Ed.) 3, 617 (1964).

from Eq. 4 to be $0{\cdot}5_7$ ev while Batley and Lyons,[10] using the same method, have given values of $2{\cdot}0_1$ and $1{\cdot}5_3$ ev. These results cannot be considered reliable since the $0{\cdot}5_7$ and $2{\cdot}0_1$ ev values were determined from data on a single complex only, viz. the perylene–maleic anhydride complex, while the $1{\cdot}5_3$ ev value was calculated relative to the electron affinity of iodine. Iodine is a σ type acceptor and will form complexes of different configuration from those formed with maleic anhydride which is a π type acceptor. Consequently it is not valid to assume that the E term of Eq. 3 will be the same for the different types of complex. The $1{\cdot}5_3$ ev value will therefore be in error by an amount equal to the difference between the E terms for π, σ and π, π complexes. From the above results this difference would appear to be about 1·4 ev.

TABLE 3. ELECTRON AFFINITIES (EA) OF DICHLOROMALEIC ANHYDRIDE AND MALEIC ANHYDRIDE CALCULATED FROM ENERGIES OF COMPLEX ABSORPTION BAND MAXIMA.[a] REFERENCE-*p*-CHLORANIL, $EA = 1{\cdot}37$ ev[b]

Donor	*p*-Chloranil	DCMA[c]		MA[d]	
	$h\nu_{CT}$(ev)	$h\nu_{CT}$(ev)	EA(ev)	$h\nu_{CT}$(ev)	EA(ev)
Toluene	3·34	4·16	0·55	—	—
m-Xylene	3·08	3·95	0·50	4·39	0·06
Mesitylene	2·89	3·70	0·56	4·12	0·14
Durene	2·56	3·45	0·48	3·97	−0·04
Pentamethylbenzene	2·53	3·34	0·56	3·74	0·16
Hexamethylbenzene	2·40	3·19	0·58	3·62	0·15
1,2,4 Trimethoxybenzene	2·19	2·98	0·56	—	—
Naphthalene	2·59	3·48	0·48	3·82	0·14

[a] Solvent-carbon tetrachloride, [b] Ref. 9.
[c] Dichloromaleic anhydride, [d] Maleic anhydride.

The electron affinities of the anhydrides reflect their relative electron acceptor properties. Substitution of chlorine into the anhydride ring enhances the electron acceptor ability and increases the electron affinity by about 0·4 ev. This value is comparable to the difference in electron affinity between *p*-benzoquinone ($0{\cdot}7_7$ ev) and 2,3 dichlorobenzoquinone (1·1 ev)[9].

EXPERIMENTAL

Materials. Carbon tetrachloride, Hopkins and Williams "Spectrosil" grade was used without further purification. Toluene, mesitylene and *m*-xylene, B.D.H. were distilled before use and respective fractions boiling 110–111°, 163–164°, 138–139° collected. Durene, pentamethylbenzene and hexamethylbenzene, B. Newton Maine Ltd., were recrystallized 3 times from EtOH, resp. m.ps 79°, 53°, 162°. Naphthalene, B.D.H., was recrystallized from EtOH, m.p. 80°. 1,2,4 Trimethoxybenzene, B. Newton Maine Ltd., was distilled and the fraction boiling 86–90° collected. Dichloromaleic anhydride, L. Light and Co., was recrystallized 3 times from pet. ether (60–80°) and stored under vacuum, m.p. 120°. Maleic anhydride, B.D.H., was recrystallized from $CHCl_3$, vacuum sublimed, and stored under vacuum, m.p. 60°.

Spectrophotometric determinations. The absorption spectra and optical density measurements were recorded on a Unicam S.P. 500 spectrophotometer using 1 cm silica cells sited in a thermostated cell holder. Stock solutions of dichloromaleic anhydride and the particular hydrocarbon under study were prepared just prior to use. For each hydrocarbon–dichloromaleic anhydride system 5 sets of solutions were prepared. In each set the dichloromaleic anhydride concn. was kept constant in the

[10] M. Batley and L. E. Lyons, *Nature, Lond.* 196, 573 (1962).

range 1×10^{-3} to 3×10^{-1} M for durene and pentamethylbenzene and 3×10^{-4} to 7×10^{-4} M for hexamethylbenzene while the hydrocarbon concn. was varied over the range 3×10^{-2} to $1{\cdot}5 \times 10^{-1}$ M for durene and pentamethylbenzene and 3×10^{-3} to 1×10^{-2} M for hexamethylbenzene. A hydrocarbon solution of the same concn. as the hydrocarbon in the solution under study was used as the reference. Where necessary the measured optical densities were corrected for the absorbance of dichloromaleic anhydride using Klaboe's procedure.[11] All solutions were prepared at room temp using CCl_4 as solvent, and concns were corrected to the temp of measurement.

The λ_{max} for complex absorption bands in hydrocarbon–maleic anhydride and hydrocarbon–dichloromaleic anhydride systems were determined by making up solutions of known concn. in CCl_4 and plotting the absorption spectra of these solutions with a hydrocarbon solution of the same concentration as reference.

Acknowledgements—The author wishes to thank Mr. F. Haggarty for help with part of the experimental work.

[11] P. Klaboe, *J. Amer. Chem. Soc.* 84, 3458 (1962).

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The electron donor ability of fumaronitrile

(*Received* 28 *April* 1966)

Abstract—Evidence for the formation of complexes between fumaronitrile and iodine monochloride is given by NMR, infra-red and visible absorption spectra.

ETHYLENIC nitriles act in charge transfer complexation either as electron donors or electron acceptors dependent upon the number of cyano groups in the molecule. Acrylonitrile acts as an electron donor via the lone pair electrons on the nitrogen atom [1] while tetracyanoethylene acts as an electron acceptor via the electron deficient ethylenic bond [2]. No information has been reported to date on the donor or acceptor properties of compounds with structures intermediate between that of acrylonitrile and tetracyanoethylene. As part of a general investigation of the donor–acceptor properties of ethylenic nitriles the complexing ability of fumaronitrile has been investigated by infra-red, visible and NMR spectroscopic methods and it is shown that fumaronitrile acts as an electron donor.

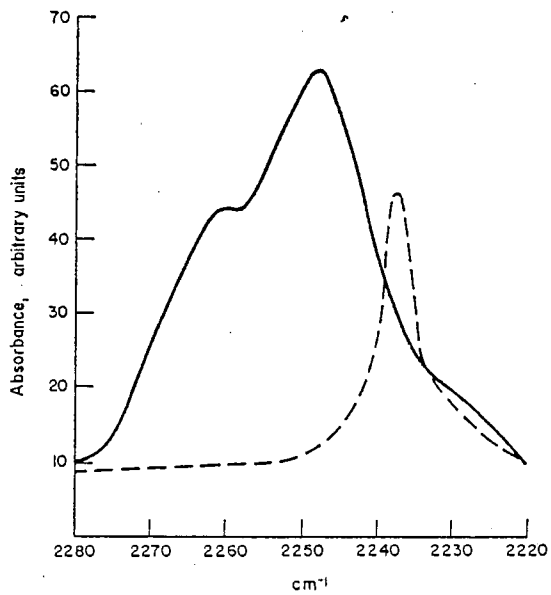

Fig. 1. The 2280–2220 cm^{-1} region of the infra-red spectra of fumaronitrile, 0·6 M (– – –), and a mixture of fumaronitrile, 0·6 M, with iodine monochloride, 2·0 M (—) in methylene dichloride.

The infra-red spectra of solutions of fumaronitrile and iodine monochloride in the region of the nitrile stretching frequency of fumaronitrile are shown in Fig. 1. It can be seen that addition of iodine monochloride to a solution of fumaronitrile in methylene dichloride results in two bands appearing on the high-frequency side of the fumaronitrile peak. This is consistent with the

[1] P. KLABOE, *Acta Chem. Scand.* **17**, 1179 (1963).
[2] R. E. MERRIFIELD and W. D. PHILLIPS, *J. Am. Chem. Soc.* **80**, 2778 (1958).

Table 1. Spectroscopic data on fumaronitrile–iodine monochloride system*

	Iodine monochloride	Fumaronitrile	Complex 1:1	Complex 2:1
—C≡N stretching frequency cm^{-1}	—	2238	2248	2261
Visible absorption $\lambda_{max.}$ (mμ)	455	—	368	
Proton resonance c/s (rel. to TMS)	—	395†	398‡ 403§	

* Solvent, methylene dichloride.
† $1{\cdot}5 \times 10^{-2}$ M fumaronitrile in CH_2Cl_2.
‡ $1{\cdot}5 \times 10^{-2}$ M fumaronitrile + 0·45 M ICl in CH_2Cl_2.
§ $1{\cdot}5 \times 10^{-2}$ M fumaronitrile + 1·41 M ICl in CH_2Cl_2.

formation of 2:1 and 1:1 fumaronitrile–iodine monochloride complexes in which the lone-pair electrons on the nitrogen are partially bonded to the iodine [3]. NMR data supports this assignment. The shift of the proton resonance in fumaronitrile to successively lower fields as the concentration of iodine monochloride in the solution is increased (Table 1) indicates a deshielding of the protons on complex formation and that there is a transfer of electron density from fumaronitrile to iodine monochloride.

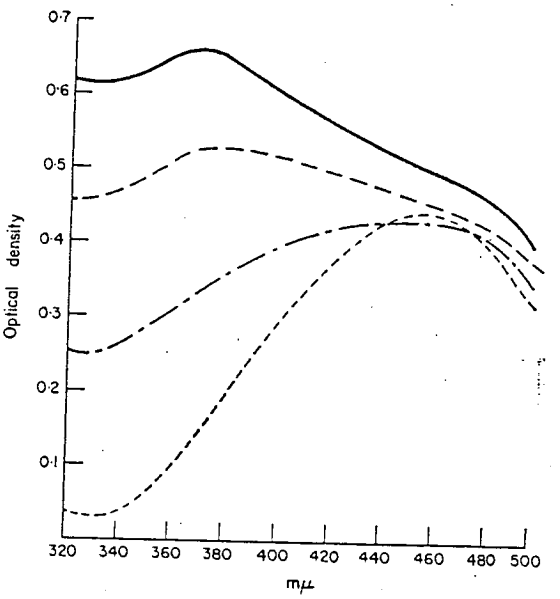

Fig. 2. The u.v.-visible absorption of mixtures of iodine monochloride ($3{\cdot}19 \times 10^{-3}$ M) with fumaronitrile, 0·00 M (. . . . .), 0·47 M (· – – ·), 1·00 M (– – –) and 2·02 M (—) in methylene dichloride (1-cm cells).

The change in the visible absorption spectrum of iodine monochloride on addition of fumaronitrile also shows that complexation occurs between the components. The absorption spectra of mixed solutions in the region 320–500 mμ are shown in Fig. 2. As the concentration of fumaro-

[3] E. Augdahl and P. Klaboe, *Spectrochim. Acta* **19**, 1665 (1963).

nitrile is increased a new band emerges on the short wavelength side of the iodine monochloride absorption. This new band may be assigned as the visible interhalogen band, blue-shifted on formation of a complex or complexes [4]. The absence of an isobestic point indicates that more than one complex is formed.

Ethylenic nitriles appear to function either solely as electron donors or electron acceptors. Although tetracyanoethylene is a strong electron acceptor it might be expected that it could also function as a donor via the lone-pair electrons on the nitrogen. This does not appear to be the case however as there is no change in the region of the —C≡N stretching frequency with added iodine monochloride. Similarly fumaronitrile does not appear to possess electron acceptor properties. Even in the presence of a strong donor such as hexamethylbenzene there is no evidence from ultra-violet and visible absorption measurements of complex formation.

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[4] A. I. POPOV and W. A. DESKIN, *J. Am. Chem. Soc.* **80**, 2976 (1958).

J. SCI. INSTRUM., 1967, VOL. 44

A photochemical reactor for quantitative studies

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MS. received 21st December 1966

Abstract. A photochemical reactor has been constructed that allows for the simultaneous irradiation of a number of samples and for each sample to receive the same fraction of incident radiation.

1. Introduction

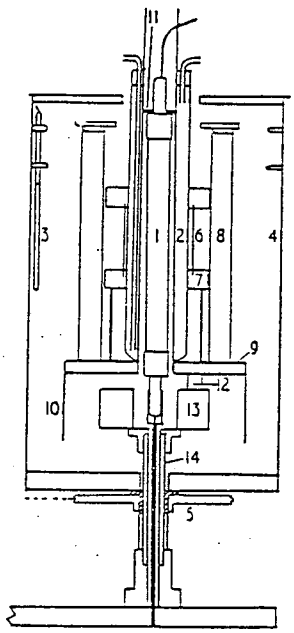
Apparatus described in the literature for the measurement of quantum yields generally only allows for irradiation of one or two samples at a time (Calvert and Pitts 1966). Many photochemical reactions have low quantum yields and in order to obtain an appreciable extent of reaction the system may have to be photolysed for a considerable length of time. This may be inconvenient, especially if a series of runs have to be carried out, since the intensity of the lamp may change during the irradiation period. If so the intensity of the lamp would have to be checked regularly during the course of the runs. In order to overcome this a photochemical reactor has been constructed which allows for the simultaneous photolysis of several samples and for each sample to receive the same fraction of incident radiation.

2. Apparatus

The apparatus consists of a mercury arc lamp mounted vertically inside a cooling jacket and a filter system. The sample tubes are positioned round the inside of a drum which

is rotated around the lamp-filter system in order to even out any variation in the transmission characteristics of the filter system.

The lamp 1 (see figure) is a Hanovia 1000 w medium



Photochemical reactor. 1, Lamp; 2, cooling jacket; 3, sample tubes; 4, aluminium drum; 5, pulley wheel; 6, glass filters; 7, filter mount; 8, annular space containing filter solution; 9, asbestos base plate; 10, polythene skirt; 11, separator; 12, one of four separators to create a gap for cooling air; 13, Perspex mounting block; 14, stationary section of plain bearing.

pressure mercury arc. It is cooled by circulating water through the cooling jacket 2 and by drawing air over the lamp with a variable-speed fan attached by wide-bore tubing to the top of the cooling jacket. The filter system consists of sections of glass filter 6 (72 mm × 72 mm × 2 mm thick) positioned round the cooling jacket and a filter solution contained in the annular space between two cylindrical Pyrex tubes (12 cm and 17 cm outer diameter, 25 cm in height, 2 mm thick) which were glued to an asbestos base plate. The part of the cooling jacket not covered by the glass filters is blackened, and a black polythene skirt 10 attached to the asbestos base plate to prevent any unfiltered light from reaching the samples. The sample tubes (9 mm outer diameter, 1 mm thick) are of Pyrex and up to 36 tubes can be mounted inside the aluminium drum 4. The drum (29 cm outer diameter, 44 cm in height) is blackened on the inside and mounted on a plain bearing (marked with hatching in the figure) attached to a pulley wheel 5. The pulley wheel is driven by an electric motor fitted with a reduction gearing at 4 rev min^{-1}.

3. Results

The variation in the amount of radiation incident upon different sample tubes was measured by irradiating a solution of benzophenone in isopropyl alcohol (Pitts *et al.* 1959), contained in tubes positioned round the drum, and determining the amount of benzophenone reacted in each tube. A 0·0382 M solution of benzophenone in isopropyl alcohol was used and each of ten sample tubes was filled to the same height (13 cm) with solution. The filter system consisted of water (20 mm path length), an OVI glass filter (2 mm thick, Precision Optical Co. Ltd.) and a saturated aqueous copper sulphate solution (20 mm path length). The system had a maximum transmission of 60% at 3850 Å. The samples were photolysed for two hours and the amount of benzophenone reacted in each tube was determined by measuring the absorbance of the solutions, after appropriate dilution, at 3800 Å. The mean extent of reaction was 14·95% and the maximum deviation from the mean was ±0·56%.

4. Conclusions

The results show that the reactor is suitable for making quantitative measurements simultaneously on different samples. The intensity of the light incident upon the samples could be determined by photolysis of actinometer solutions in the sample tubes, and quantum yields could be obtained if the reactant system were photolysed along with the actinometer solutions.

Acknowledgments

The authors thank Mr. R. Bowers for technical assistance.

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PITTS, J. N. *et al.*, 1959, *J. Amer. Chem. Soc.*, 81, 1068–77.

Tetrahedron Letters No.42, pp. 4401–4404, 1968. Pergamon Press. Printed in Great Britain.

THE PHOTOREACTIVE STATES OF 9-ANTHRALDEHYDE

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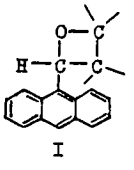
(Received in UK 12 July 1968; accepted for publication 23 July 1968)

The recent publication by Yang and Loeschen (1) on the photochemical reaction of 9-anthraldehyde with 2,3-dimethyl-2-butene prompts us to report our findings on this and other systems involving 9-anthraldehyde. We have studied the photo-reaction of 9-anthraldehyde with 2,3-dimethyl-2-butene under experimental conditions (λ = 3660°A, temp. = 30–35°) which differ from those of Yang et al. (2). Whereas Yang (3) has found that the oxetane I was the major product of the reaction when light of wavelength shorter than 400 mμ was used, we have found that under our conditions the pinacol II and polymeric material are the major products of the reaction and that oxetane I and also the dimer of 9-anthraldehyde are minor products. Pinacol II was also formed in the photo-reaction of 9-anthraldehyde with toluene under our experimental conditions along with the dimer of 9-anthraldehyde, polymeric material and dibenzyl.



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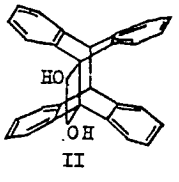

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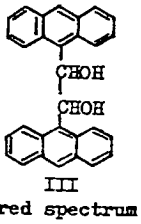
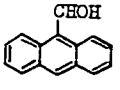
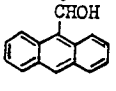


III

Pinacol II was characterised by elemental analysis, the infrared spectrum (–OH stretching band at 3460 cm^{-1}), the ultraviolet spectrum (lack of 'anthracene type' absorption in the region 300–400 mμ) and the mass spectrum (molecular ion peak m/e 414, base ion peak m/e 207). Pinacol II is most probably formed in the reaction sequence

(9-anthraldehyde) + hν ⟶ (9-anthraldehyde)* (1)

(9-anthraldehyde)* + RH ⟶  + R• (2)

2  ⟶ Pinacol III (3)

Pinacol III + hν ⟶ Pinacol II (4)

Absorption of light energy by pinacol III will lead to pinacol II (step 4) by a process analagous to that by which 1,2-bis(9-anthryl)ethane is linked across the 9,10 positions of the anthracene systems (4).

The relative product yields in the reaction of 9-anthraldehyde with 2,3-dimethyl-2-butene depend upon the wavelength of the incident light, and under our conditions as under those of Yang et al. (3), the major product of the reaction when light of wavelength longer than 410 mμ is used is the dimer of 9-anthraldehyde.

The ability of an aryl ketone to abstract hydrogen from a substrate is dependent upon the nature of the reactive triplet state of the ketone; compounds with reactive n,π^* states are photoreduced with ease (5) while those with reactive π,π^* triplet states are not readily photoreduced (6). Since the photoreactive state of 9-anthraldehyde abstracts hydrogen from substrates, such as 2,3-dimethyl-2-butene and toluene, which are not attacked by aryl ketones with reactive π,π^* triplet states, it would appear that the reactive state of 9-anthraldehyde is an n,π^* triplet state. Also, the fact that the photoreduction reactions are inhibited by triplet state quenchers (see Table I) is indicative that the reactive state is a triplet state and not a singlet state as has been previously suggested (7). The energy of the reactive triplet state of 9-anthraldehyde has been estimated by means of the quenching experiments reported in Table I. Benzene solutions containing 0.01M 9-anthraldehyde, 0.68M 2,3-dimethyl-2-butene and quencher were degassed and irradiated with monochromatic light of 366 mμ (8). The quantum yield for the disappearance of 9-anthraldehyde was determined by spectrophotometric measurement of the concentration of 9-anthraldehyde before and after reaction and by measuring the light energy absorbed by the reactant solutions using a benzophenone-benzhydrol actinometer (9). The quantum yield values given below are corrected for the small percentage of light absorbed by the quencher.

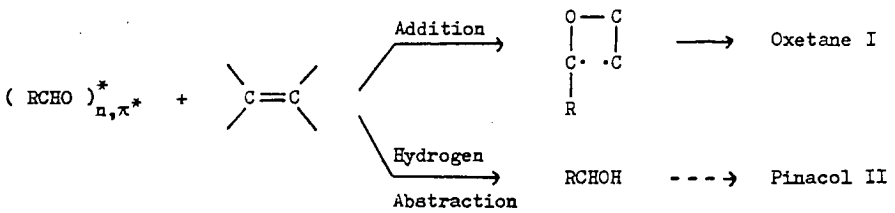
TABLE I

Quencher	Conc.	E_T (Kcal/mole)	ø
None	-	-	0.012
Naphthalene	0.80M	60.9	0.012
2-Acetonaphthone	0.02M	59.3	0.011
1-Naphthaldehyde	0.02M	56.3	0.010
Benzil	0.02M	53.7	0.009
Pyrene	0.02M	48.7	0.009
Azulene	0.02M	31-39	0.009

As can be seen from Table I there is a small but significant decrease in the quantum yield for the disappearance of 9-anthraldehyde in the presence of 2-acetonaphthone, 1-naphthaldehyde, benzil, pyrene and azulene. The reaction is not quenched by naphthalene, even when present in high concentration, indicating that the energy of the reactive triplet state is similar to or lower than that of naphthalene. If the energy of the reactive triplet state is close to that of naphthalene then the rate of reversible energy transfer from the triplet state of naphthalene to the reactive triplet state may be such that quenching would not be observed under the conditions of our experiments. Coupled transitions between the reactive triplet state of 9-anthraldehyde and the triplet state of naphthalene would be expected to occur with reasonable probability even if the difference between the energies of the lowest vibrational levels of the two states was of the order of 3 Kcal/mole. Yang and Loeschen have shown by means of photosensitisation experiments (1) that the energy of the reactive triplet state must be above 58 Kcal/mole and this result taken in conjunction with the present results places the energy limits for the reactive triplet state of 9-anthraldehyde between 58 to 64 Kcal/mole. These limits for the energy of the reactive triplet state provide additional evidence that this state is n,π^* in character since aromatic carbonyl compounds with reactive π,π^* triplet states of similar energy are unable to abstract hydrogen from substrates such as toluene and isopropanol (6).

Yang et al. (10) have suggested that in the photoreaction of 9-anthraldehyde with 2,3-dimethyl-2-butene there are two excited states of 9-anthraldehyde involved in the reaction leading to oxetane I; one state being responsible for 77% of the oxetane formed and the other for 23%. The nature of these states is not known conclusively but Yang and Loeschen's evidence from photosensitisation experiments (1) suggests that both states lie in the triplet manifold. The recent observation (11) that the energy of the lowest triplet state of 9-anthraldehyde is 43.5 Kcal/mole above the ground state excludes the possibility that this state is active in either the reaction forming oxetane I or that leading to pinacol II. In view of the present evidence which indicates that the reactive state in the reaction leading to pinacol II is an n,π^* triplet state, it is reasonable to assume that this state is responsible for the 77% of the oxetane formed under the conditions of Yang and Loeschen's experiments. This is supported by previous work of Yang et al. (3) which indicates that the formation of oxetanes from 1-naphthaldehyde and 2-naphthaldehyde, which possess lowest π,π^* triplet states, occurs via an n,π^* species. Thus it would appear that the n,π^* triplet state of 9-anthraldehyde,

like that of other carbonyl compounds (12), can either add across the double bond of an olefin or else abstract a hydrogen atom (see scheme below). However the possibility that hydrogen abstraction occurs via an n,π^* triplet state while addition across the double bond occurs mainly via a π,π^* triplet state cannot be ruled out.



At elevated temperatures the biradical intermediate in the oxetane forming sequence may well readily dissociate before ring closure can occur to form starting materials in the ground state. Consequently the hydrogen abstraction process would become more predominant at elevated temperatures, especially since the activation energy for this process would be expected to be higher than that for the addition process.

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Perturbation of singlet–triplet transitions in aromatic carbonyl compounds

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Abstract—Singlet–triplet transitions in aromatic carbonyl compounds with lowest π, π^* triplet states are enhanced by the presence of oxygen while singlet–triplet transitions in aromatic carbonyls with lowest n, π^* triplet states are unaffected. The oxygen perturbation technique thus provides a simple method for characterising the lowest triplet state of aromatic carbonyl compounds.

INTRODUCTION

PHOTOCHEMICAL reactions often proceed via the lowest triplet states of molecules and in many cases the photoreactivity of the molecule can be correlated with the nature of the lowest triplet state [1]. In view of the role of the triplet state in photochemistry it is important that the nature of the lowest triplet state be characterised.

Information on triplet states can either be obtained from triplet → singlet emission spectra [2, 3] or from singlet → triplet absorption spectra [4]. The former method has been utilised to yield data on both the nature of the triplet states from which emission occurs [2, 3] and on the energy levels of the emitting states [5] while the latter method has been used in the determination of energy levels of triplet states [4]. Since singlet–triplet absorption spectra can often be readily observed in the presence of a paramagnetic molecule under high pressure [4] it was proposed to investigate this method as a means of characterising the lowest triplet states of molecules. Aromatic carbonyl compounds were chosen for this study since a great deal of information has been accumulated on the properties of triplet states in such compounds.

EXPERIMENTAL

The high pressure absorption cell consisted of a brass tube (9·0 cm long) with silica windows (1·6 cm o.d. and 6 mm thick) mounted on each end between polytetrafluorethylene gaskets by means of a hollow brass screw cap. The overall path length of the cell was 8·5 cm. A high pressure valve and a filling port were mounted

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on the side of the tube. The valve could be joined via a pressure gauge to a cylinder of oxygen. The cell could be mounted in a 10 cm cell-holder in the sample compartment of a Unicam SP.800 spectrophotometer. Spectra were obtained at atmospheric pressure and at a pressure of 100 atm of oxygen.

The solutes were the purest available commercially and were either distilled or twice recrystallised before use. The solvents used were either Analar or Spectrosol grade.

Results and Discussion

The spectra shown in Figs. 1–3 illustrate the effect of oxygen on the absorption of several aromatic carbonyl compounds. The noteworthy feature is that compounds

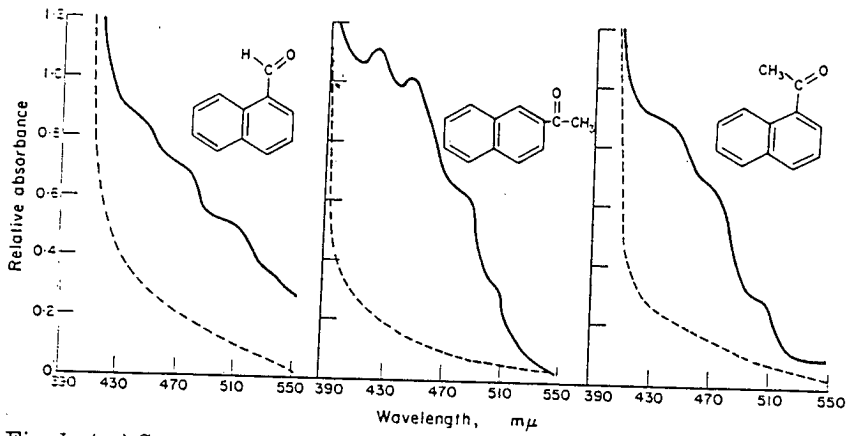

Fig. 1. (---) Spectrum at atmospheric pressure; (—) spectrum under 100 atm of oxygen. 1-naphthaldehyde, 0·20 *M* in n-hexane; 2-acetonaphthone, 2·00 *M* in chloroform; 1-acetonaphthone, 1·00 *M* in chloroform. Path length 8·5 cm. Reference—attenuator.

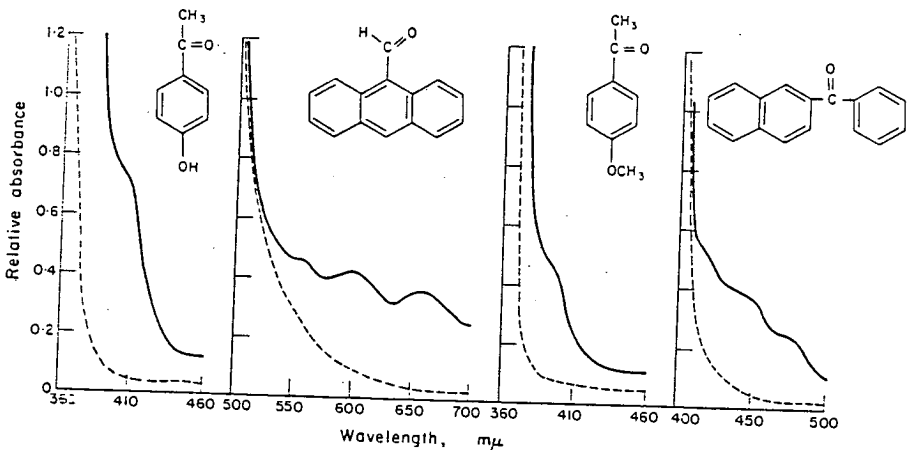

Fig. 2. (---) Spectrum at atmospheric pressure; (—) spectrum under 100 atm of oxygen. 4-hydroxyacetophenone, 0·80 *M* in chloroform; 9-anthraldehyde, 0·58 *M* in benzene; 4-methoxyacetophenone, 0·50 *M* in ethanol; 2-naphthyl phenyl ketone, 0·50 *M* in chloroform. Path length 8·5 cm. Reference—attenuator.

which have lowest π, π^* triplet states (see Table 1) show an enhancement of the S–T transition in the presence of oxygen while compounds with lowest n, π^* triplet states are unaffected. The results obtained for compounds whose lowest triplet states have been assigned as π, π^* are given in Table 1.

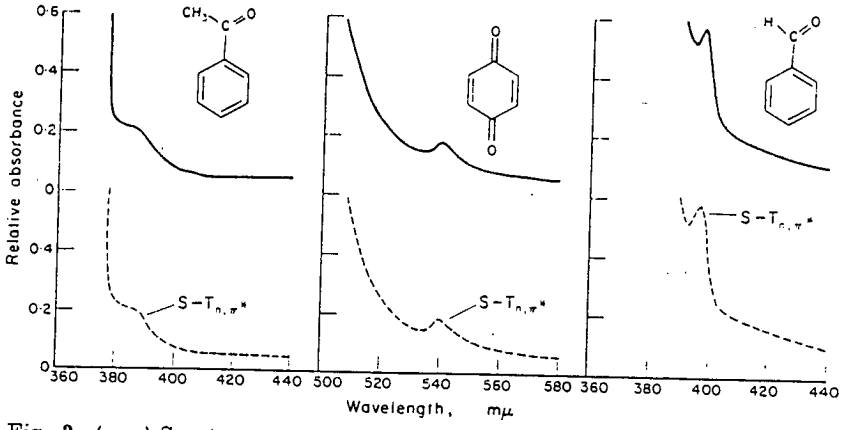

Fig. 3. (- - -) Spectrum at atmospheric pressure; (—) spectrum under 100 atm of oxygen. Acetophenone, 0·20 M in n-hexane; p-benzoquinone, 0·03 M in n-hexane; benzaldehyde, 0·70 M in n-hexane. Path length 8·5 cm. Reference—attenuator.

Table 1. Perturbation of S–T transitions in aromatic carbonyl compounds with lowest π, π^* triplet states

Compound	λ_{max} of enhanced bands (mμ)	Energy of lowest triplet level (kcal/mole) Exp.	Lit.	Assignment of lowest triplet state References
4-hydroxyacetophenone	405	70·6	72·4*	[3]
4-methoxyacetophenone	397	72·0	76·7*	[3]
1-acetonaphthone	447, 475, 506	56·5	56·4†	[13]
2-acetonaphthone	422, 450, 486	58·8	59·3†	[13]
2-naphthyl phenyl ketone	423, 450, 480	59·6	59·6†	[13]
1-naphthaldehyde	444, 474, 510	56·1	56·3†	[13]
9-anthraldehyde	558, 600, 658	43·5	—	[14]

* Ref. [3].
† Ref. [5].

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It can be seen from Table 1 that the energies of the lowest triplet states as calculated from the position of the longest wavelength S–T absorption bands agree well with the literature values. In cases where the S–S absorption band did not lie close to the lowest energy S–T transition vibrational structure could be observed. The spacing of the vibrational levels in compounds containing the naphthalene moiety was approximately 1400 cm^{-1} which is similar to that observed for naphthalene [4]. The lowest triplet level of 4-hydroxybutyrophenone has been assigned as π, π^* [6] but no enhanced S–T bands could be observed in the spectrum (not shown). At the concentrations required to observe S–T transitions the intensity of the S–S band in 4-hydroxybutyrophenone in the region in which the S–T transitions would occur is high and the weak S–T transitions are hidden.

The S–T transitions in 2-acetonaphthone, 2-naphthyl phenyl ketone and 9-anthraldehyde are intensified in the presence of iodobenzene and can be observed directly when iodobenzene is used as solvent. The enhanced bands are at the same position as the bands observed in the presence of oxygen but the intensities of the bands in iodobenzene are about one-third that for the bands observed when the oxygen pressure was 100 atm for the same concentration of solute and path length. Intensification of S–T_{π,π^*} transitions by solvents containing heavy atoms has been previously observed for aromatic hydrocarbons [7] and aromatic carbonyl compounds [3]. As the enhancement in heavy atom solvents is weak as compared to that in the presence of oxygen, the oxygen perturbation method is to be preferred for the observation of S–T_{π,π^*} transitions.

Acetophenone, p-benzoquinone and benzaldehyde which have lowest n, π^* triplet states do not show enhancement of S–T transitions in the presence of oxygen at 100 atm. Figure 3 illustrates that the S–T transitions in acetophenone, benzaldehyde and p-benzoquinone can be observed directly and that there is no oxygen effect on these transitions. The absence of oxygen perturbation is in accord with previous experimental findings for the effect of heavy atom solvents on the intensity of S–T_{n,π^*} transitions [3] and for the effect of oxygen at atmospheric pressure on the S–T_{n,π^*} transition in benzaldehyde [8].

It is of interest to note that S–T_{n,π^*} transitions in pyrazine [9] and in acridine [4] are enhanced by oxygen. In these systems as in the aromatic carbonyl systems with lowest π, π^* triplet states the half-vacant bonding and anti-bonding orbitals are specifically associated with the aromatic ring and obviously this situation favours enhancement of S–T transitions. Two theories have been proposed to account for the intensification of the S–T absorption by a perturber molecule. MURRELL [10] and TSUBOMURA and MULLIKEN [11] have suggested that the intensification is due to intensity-borrowing of the S–T transition from a charge transfer transition in an aromatic hydrocarbon-perturber complex, while HOIJTINK [12] has attributed the effect to intensity-borrowing from the corresponding S–S transition in the aromatic hydrocarbon, the magnitude of the enhancement being dependent on the extent of electron exchange between the aromatic molecule and the paramagnetic perturber. The results obtained in the present work do not allow a choice to be made between the two theories and the relative importance of the exchange or charge transfer mechanism must still remain an open question.

Since S–T transitions of aromatic carbonyl compounds with lowest π, π^* triplet

states are enhanced by oxygen whilst $S–T$ transitions in aromatic carbonyls with lowest n, π^* triplets are unaffected, the oxygen perturbation technique provides a method for characterising the lowest triplet states of such compounds. The method has the advantage over phosphorescence methods [5] and phosphorescence excitation methods [3] in that the spectra can be obtained in a routine manner without specialised equipment.

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Electron affinity of maleic anhydride, diiodomaleic anhydride and dichloromaleic anhydride

by G. L. O. Davies and C. H. J. Wells

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It is well known that anhydrides act as electron acceptors in the formation of charge-transfer complexes with aromatic hydrocarbons[1] and that the ability to form complexes is dependent upon the electron affinity of the anhydride.[2] Nevertheless the complexing abilities of maleic anhydride and halogenated derivatives of maleic anhydride are not well defined, owing to lack of data on the electron affinities of halogenated derivatives and to the uncertainty in the reported values for the electron affinity of maleic anhydride.[2–4] The electron affinities of maleic anhydride (MA), diiodomaleic anhydride (DIMA) and dichloromaleic anhydride (DCMA) reported here were calculated from the energy of the charge-transfer transition in complexes formed with pyrene and hexamethylbenzene using equations derived by Briegleb.[3] The energies of the charge-transfer transitions ($h\nu_{CT}$) in the complexes are listed in Table I and the calculated values of the electron affinities are given in Table II. The energies of the charge-transfer transition in complexes of *p*-chloranil with pyrene and hexamethylbenzene are also included in Table I since these values are used in the calculation of electron affinities by method II.

Table I

$h\nu_{CT}$ values for MA, DIMA, DCMA and p-chloranil complexes in carbon tetrachloride

Donor / *Acceptor*	*Hexamethylbenzene* $h\nu_{CT}$ *ev*	*Pyrene* $h\nu_{CT}$ *ev*
MA	3·62	—
DIMA	3·26	3·02
DCMA	3·15	2·91
p-Chloranil	2·40	2·04

Table II

Electron Affinities (ev) of MA, DIMA and DCMA

Donor	*Method of calculation*[a] *I*	*II*	*III*	*IV*
MA complexes				
Hexamethylbenzene	—	0·15	0·01	0·08
DIMA complexes				
Hexamethylbenzene	—	0·51	0·38	0·44
Pyrene	0·40	0·39	0·42	0·49
DCMA complexes				
Hexamethylbenzene	—	0·62	0·50	0·55
Pyrene	0·51	0·50	0·54	0·60

[a] Reference 3: I – eqn (23'); II – eqn (25); III – eqns (28') and (30); IV – eqn (33)

The mean values of the electron affinities of MA, DIMA and DCMA calculated by methods I, II, III and IV are 0·08, 0·43 and 0·55 *ev* respectively. These values indicate that the relative acceptor strengths of the anhydrides lie in the order DCMA>DIMA>MA. The interesting feature is the marked increase in electron affinity on substitution of iodine or chlorine into the anhydride ring system and the relatively small difference in electron affinity between the iodo and chloro derivatives. This effect is paralleled in the quinone system where the electron affinities of *p*-benzoquinone, *p*-iodanil and *p*-chloranil are 0·77, 1·36 and 1·37 *ev* respectively.[3]

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The infra-red spectra of some vinyl, methyl and isopropenyl substituted *cyclo*butanes

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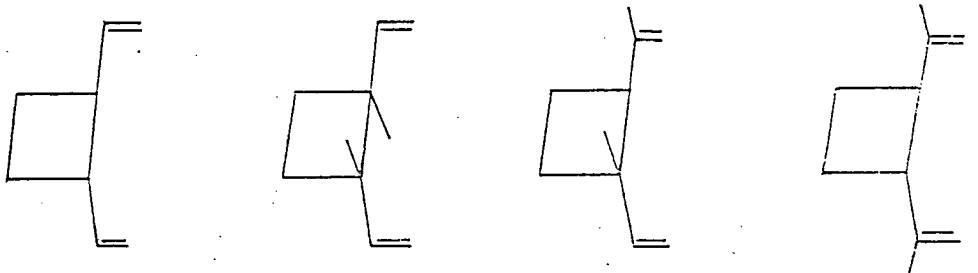
(*Received* 24 *November* 1967)

Abstract—The infra-red spectra (3500–400 cm^{-1}) of *trans*-1,2-divinyl*cyclo*butane, *trans*-1,2-dimethyl-1,2-divinyl*cyclo*butane, *trans*-1-isopropenyl-2-methyl-2-vinyl*cyclo*butane and *trans*-1,2-diisopropenyl*cyclo*butane are reported. Assignments for the principal vibrational frequencies are given.

Introduction

Some early assignments [1] of infra-red frequencies associated with various aliphatic hydrocarbon groupings have become well established in the literature of spectral correlations. It is important to assess the range of validity of such correlations, particularly when a hydrocarbon contains several types of groupings (including cyclic systems). In the present work the infra-red spectra of *trans*-1,2-divinyl*cyclo*butane (I), *trans*-1,2-dimethyl-1,2-divinyl*cyclo*butane (II), *trans*-1-isopropenyl-2-methyl-2-vinyl*cyclo*butane (III) and *trans*-1,2-diisopropenyl*cyclo*butane (IV) have been studied.



I II III IV

Comparison of the spectra of compounds I–IV enable a number of unequivocal assignments to be made. These are considered in relation to the characteristic frequencies currently attributed to methyl, vinyl, vinylidene and *cyclo*butane groupings.

Experimental

Compounds I–IV were prepared by the method of Hammond *et al.* [2] and were purified by gas-phase chromatography.

Infra-red spectra were recorded between 400 and 3500 cm^{-1} on a Grubb Parson "Spectromaster" spectrometer. This instrument was calibrated with indene [3] and

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all the frequencies reported should be accurate to better than 5 cm^{-1}. Each sample was examined as a 10% v/v solution in carbon tetrachloride at 0·1 mm path length and as a liquid film at 0·1 mm path length. In each case the spectra of the sample in the two states were the same except that additional weak bands were observed in the spectra of the liquid state.

Discussion

The substituents on the *cyclo*butane ring in compounds I, II, III and IV may take up a number of different possible conformations. The most probable conformation in compounds I, II and IV has a two-fold rotation axis of symmetry and the molecules are likely to belong to the C_2 point group. All vibrations are infra-red active belonging either to species A or B (symmetric and antisymmetric to the two-fold rotation axis respectively). It follows [4] that compound I will have 54 fundamental vibrations (28 a and 26 b), compounds II and IV will have 72 fundamental vibrations (37 a and 35 b). Compound III will also have 72 fundamental vibrations but no distinction can be made between them using symmetry considerations. In these compounds a large number of vibrational frequencies will overlap, others will be very weak and some will occur at very low frequencies. It is unlikely that any detailed assignments can be made to the a and b symmetry species. The frequencies of the absorption bands of compounds I, II, III and IV are compared and assigned in Table 1. It will be convenient to discuss the spectra of these compounds under the following headings.

Olefinic groups

The olefinic $=CH_2$ asymmetric stretching frequencies are assigned between 3084 and 3087 cm^{-1} in all four compounds: no difference is observed between these frequencies in the vinyl and vinylidene group. The $=CH_2$ symmetric frequency is seldom assigned; however, Nakanishi [5] suggested that this mode absorbs at 2975 cm^{-1} and consequently bands in the 2969–2980 cm^{-1} region of the spectrum of compounds I, II, III and IV are probably due to this mode although strongly overlapped by other C—H stretching modes. The —CH= stretching frequency in compounds I, II and III is observed in the 3060–3072 cm^{-1} region. This is significantly higher than the 3010–3040 cm^{-1} region in which absorptions from this mode occur in acyclic vinyl compounds [6]. Two C=C stretching modes are observed for compound III and comparison with compounds I, II and IV reveal that the vinylidene C=C stretching mode is at higher frequency than that due to the vinyl C=C stretching mode. The presence of only one C=C stretching frequency in compounds I, II and III (together with the absence of any doubling of other olefin frequencies) is evidence in favour of a single conformation for each molecule with the olefinic groups occupying equivalent environments. It is expected that the a and b modes are superimposed due to the large separation of the olefinic groups in these molecules. In-plane deformations of the vinyl C—H groups are assigned at 1414 cm^{-1} and also a weak band near 1290 cm^{-1} in compounds I and II is probably associated with these modes. The in-plane deformation of the vinylidene C—H group has previously

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Table 1. Comparison of assigned frequencies (cm^{-1})* for some vinyl, methyl and isopropenyl substituted *cyclo*butanes

I	II	III	IV	Assignments
3084 m	3087 m	3087 m	3084 m	$=CH_2$ asym st.
3072 sh	3061 w	3061 vw		=CH— st. (vinyl)
2996 sh	2996 sh	3001 sh	3008 w	ring C—H asym st.
2980 s	2969 s	2969 s	2969 s	$=CH_2$ sym. st.
2940 m	2939 sh	2939 s	2942 s	CH_3 and ring C—H asym. st.
2905 m	2905 m	2910 w	2914 s	
2866 m	2866 m	2873 m	2866 m	CH_3 and ring C—H sym. st.
1826 w	1826 w	1826 w		$2 \times 911 = 1822$
		1783 w	1783 w	$2 \times 886 = 1772$
		1640 m	1643 m	C=C st. (vinylidene)
1635 s	1637 m	1632 m		C=C st. (vinyl)
1460 w				ring C—H asym. def.
	1456 m	1449 m	1451 m	CH_3 asym. def.
1441 m	1449 m	1439 m	1439 m	ring C—H asym. def.
1422 m				
1414 m	1414 m	1414 m		C—H in-plane def. (vinyl)
	1372 m	1372 m	1374 m	CH_3 sym. def.
1289 w	1292 w			C—H in-plane def. (vinyl)
		1276 w	1292 w	C—H in-plane def. (vinylidene)
1235 w	1266 w	1242 m	1250 m	C—C ring st.
	1218 w	1220 m	1215 w	
	1200 w			C—C, C—Me st.
	1162 w			
1111 w	1110 w	1116 w	1100 m	C—C ring st.
	1089 m			
	1052 w	1042 m	1004 w	C—C, C—Me st.
990 s	998 s	998 m		—HC=CH— out-of-plane twist (vinyl)
912 s	910 s	910 s		$=CH_2$ wag (vinyl)
		885 s	887 s	$=CH_2$ wag (vinylidene)
667 m	684 m	680 m		
629 w				ring def.
588 w	566 w	546 w		—CH=CH_2 wag (vinyl)

* Frequencies quoted are for 10% v/v solutions in carbon tetrachloride.
s = strong, m = medium, w = weak, sh = shoulder.

been assigned to the 1410–1420 cm^{-1} region [7]. The intensity pattern for bands in this region for compounds I, II, III and IV clearly establishes that the in-plane vinylidene C—H deformations occur elsewhere and weak bands at 1276 and 1292 cm^{-1} in compounds III and IV are assigned to these modes. The out-of-plane deformations are readily assigned from their characteristic frequencies and intensities. The three out-of-plane modes of the vinyl group are very similar to those in propene (990, 912, 577 cm^{-1}) [8] and the forms of these vibrations have been the subject of normal co-ordinate calculations [9].

Cyclobutane groups

Vibrations due to the *cyclo*butane system should be more clearly observed in compound I than in compounds II, III and IV since overlapping methyl absorptions are absent in the former. Furthermore vibrations associated with the vinyl group are less likely to couple with the ring vibrations than those due to a methyl group. It has been shown [7] that cyclic C—H stretching modes absorb at higher frequencies

[7] H. L. McMurray and V. Thornton, *Anal. Chem.* **24**, 31B (1952).
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than linear C—H stretching modes. The present work indicates a series of bands between 2866 and 3008 cm^{-1} in all four compounds. These are particularly well-defined in compound I and are assigned to the symmetric ring C—H stretching modes (2866, 2905 cm^{-1}) and asymmetric ring C—H stretching modes 2940 and 2996 cm^{-1}. The absorption near 3000 cm^{-1} is probably the most reliable band in the spectrum for indicating the presence of a *cyclo*butane ring. This is because remaining fundamental vibrations are in regions of the spectrum where other hydrocarbon frequencies occur. For example ring C—H deformation modes observed between 1439 and 1450 cm^{-1} in compounds I–IV are overlapped by CH_3 modes in compounds II–IV. Similarly bands at 910–920 cm^{-1} which have been assigned to the ring vibrations of mono-alkyl *cyclo*butanes [10] are overlapped by absorptions of the vinyl group. Ring stretching vibrations are assigned to bands in the region 1100–1116 cm^{-1} and 1235–1266 cm^{-1} in the present work; these are likely to be coupled with C—vinyl stretching modes. Bands between 669 and 686 cm^{-1} are probably due to ring deformation modes.

Methyl groups

The two methyl groups in compounds II, III and IV produce a general broadening of bands in the C—H stretching region which prevents the assignment of CH_3 stretching modes. However, CH_3 deformation modes are clearly observed between 1449 and 1456 cm^{-1} (asymmetric) and 1322–1374 cm^{-1} (symmetric). Comparison of the spectra of these compounds suggest weak or medium bands in the region 1004–1089 cm^{-1} and 1162–1218 cm^{-1} are due to coupled C—C modes.

Acknowledgement—Thanks are due to the Science Research Council for grants for the purchase of spectroscopic equipment and a preparative gas-phase chromatograph.

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RESEARCH NOTE

Solvent effects on the carbonyl stretching frequency of 1-naphthaldehyde

(*Received* 25 *March* 1968)

Abstract—The solvent-induced shift of the C=O stretching band of 1-naphthaldehyde in the 1-naphthaldehyde-iodine monochloride complex is greater than that for 1-naphthaldehyde in the free state. This is accounted for in terms of the difference between the dipole moment of the molecule in the two states.

THE solvent-induced frequency shifts in the stretching vibrations of various types of linkage has been extensively studied and explanations for the effect have been given in terms of specific solute–solvent interactions [1, 2], non-specific dispersion forces and bulk dielectric effects of the medium [3, 4]. In the case of the stretching vibration of the X—H group the main contributing factor to the frequency shift is specific solute–solvent interaction, whereas the evidence to date for the C=O group suggests that each of the above factors contributes to the solvent-induced shift. The magnitude of the shift is also determined by the strength of the dipole involved in the interaction [5, 6]. In the course of a study on charge-transfer complexation the effect of solvent on the C=O stretching frequency of 1-naphthaldehyde in the presence of iodine monochloride has been examined. This system is of interest because the C=O group is present in two states viz. the "free" state and the "complexed" state C=O----I—Cl [7], and because the strength of the dipole in the C=O group is different in the two states.

EXPERIMENTAL

1-Naphthaldehyde (Koch-Light) was purified by distillation under vacuum. Iodine monochloride (B.D.H.) was fractionally recrystallised three times. The solvents were distilled before use.

The spectra were obtained by means of a Grubb-Parsons "Spectromaster" which was calibrated using the spectrum of indene [8]. The path length of the cell was 0·1 mm. The spectrum of 1-naphthaldehyde was recorded in the region of the carbonyl absorption in each solvent with and without added iodine monochloride. The addition of iodine monochloride did not alter the position of the "free" carbonyl absorption band. The relative concentrations of 1-naphthaldehyde and iodine monochloride in the mixed solutions were adjusted to give optimum peak heights for the "free" and "complexed" carbonyl bands. The vapour phase spectrum of 1-naphthaldehyde was obtained at 150°C using a stainless steel cell with a path length of 70 mm.

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Discussion

The spectrum of 1-naphthaldehyde in the presence of iodine monochloride exhibits two bands in the carbonyl region. These bands have been assigned as arising from the stretching vibration of the "free" and "complexed" carbonyl groups; the band at higher frequency corresponding to the "free" carbonyl group [7]. It can be seen from Table 1 that, in general, the positions of these bands shift to lower frequencies as the polarity of the solvent increases. Unfortunately the range of solvents which could be used was limited on account of the reactivity of iodine monochloride.

Table 1. Effect of solvent on C=O stretching frequency (cm^{-1}) of 1-naphthaldehyde

Solvent	ν		$\Delta\nu$	
	Free	Complex with ICI	Free	Complex with ICI
Vapour	1713			
Cyclohexane	1704	1662	9	51
Diethyl ether	1699	1656	14	57
Carbon tetrachloride	1698	1657	15	56
Carbon disulphide	1697	1652	16	61
n-Butyl chloride	1697	1655	16	58
Chloroform	1691	1649	22	64
Dichloromethane	1693	1648	20	65

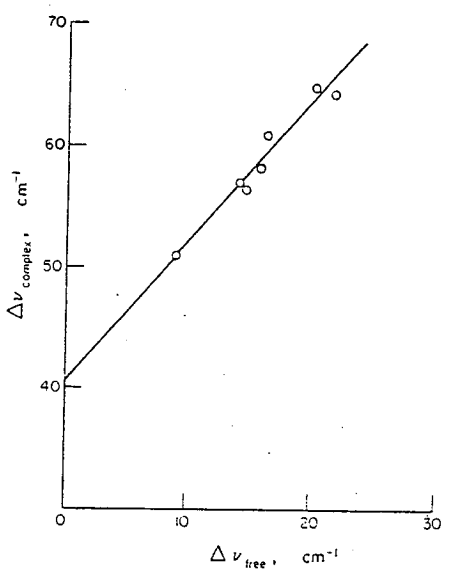

Fig. 1. Relative solvent shifts of C=O stretching band in "free" and "complexed" states of 1-naphthaldehyde.

The shifts ($\Delta\nu$) of the "free" and "complexed" carbonyl bands in the different solvents relative to the position of the free carbonyl absorption in the vapour state are given in Table 1, and the shifts for the "complexed" carbonyl band are plotted against those of the "free" carbonyl band in Fig. 1. The plot in Fig. 1 is linear and has a slope of 1·18 ± 0·16 (the error is based on lines of maximum and minimum slope). This indication that the effect of solvent on the C=O stretching vibration is greater for the "complexed" state than for the "free" state is in accord with previous findings (5) that solvent-induced shifts for stretching vibrations of

C-Halogen and C=O groups in rotational isomers are dependent upon the dipole moment of the isomer and that the larger the greater is the shift. Since the interaction between 1-naphthaldehyde and iodine monochloride involves transfer of electronic charge from the oxygen atom of the carbonyl group to the iodine atom of the interhalogen, with consequent rearrangement of the charge distribution in the carbonyl function, the dipole moment of 1-naphthaldehyde in the "complexed" state will be greater than that for the "free" state. The relatively small difference between the solvent-induced shifts for the "free" and "complexed" states is indicative of the weak nature of the bond in the charge-transfer complex formed between 1-naphthaldehyde and iodine monochloride.

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Mass Spectra of Isomers. Part I. Cyclobutanes and Cyclohexenes of Molecular Formula $C_{10}H_{16}$

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H. M. Paisley, Chemical Standards Division, National Physical Laboratory, Teddington

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Mass Spectra of Isomers. Part I. Cyclobutanes and Cyclohexenes of Molecular Formula $C_{10}H_{16}$

By E. F. H. Brittain* and C. H. J. Wells.* Department of Chemistry, Kingston College of Technology, Kingston upon Thames
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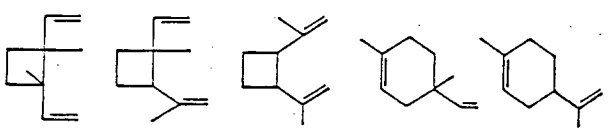
The mass spectra of a number of isomeric derivatives of cyclobutane and cyclohexene of molecular formula $C_{10}H_{16}$ have been examined and found to be similar. Metastable ions were observed for all processes except those for the formation of the ion *m/e* 68 and for cleavage of an ethylene molecule from the ring of the molecular ions. The differences in the intensities of the major peak in the spectra result from differences in stability of the molecular ions.

ALTHOUGH mass spectroscopy is of use in the identification of positional isomers [1] there are few reports on the fragmentation processes in such compounds. The work reported here describes the mass spectra of isomeric derivatives of cyclobutane and cyclohexene of molecular formula $C_{10}H_{16}$.

The mass spectral data for *trans*-1,2-dimethyl-1,2-divinylcyclobutane (I), *trans*-1-isopropenyl-2-methyl-2-vinylcyclobutane (II), *trans*-1,2-di-isopropenylcyclobutane (III), 1,4-dimethyl-4-vinylcyclohexene (IV), and 1-methyl-4-isopropenylcyclohexene (V) are listed in Table 1. The peak intensities of the ions are given as percentages of the intensity of the base peak.



(I) (II) (III) (IV) (V)

As expected, the major peaks and the positions of the metastable ions in the mass spectra are similar for all the compounds. The base peak in each spectrum is due to the ion *m/e* 68 which is readily assigned as the molecular ion of isoprene. The mass spectrum of each compound below *m/e* 68 is similar to that of isoprene; [2] consequently the discussion is limited to fragmentation processes which originate from ions with *m/e* values greater than 68. Although the same metastable ions are observed in all the spectra, indicating similar fragmentation routes, the cyclobutanes and the cyclohexenes are, for convenience, discussed separately.

Mass Spectra of Cyclobutane Derivatives.—Possible fragmentation processes for compound (I) which lead to ions having an *m/e* value greater than or equal to 68 and which yield ions having a relative intensity of 10% or more are shown in Figure 1. Where possible, these assignments are made on the basis of observation of metastable ions, *m**, as indicated in Figure 1. The fragmentation processes for compounds (II) and (III) are the same except that the position of the methyl groups and charge sites in the molecular and fragment ions differ. Metastable ions corresponding to the transitions *m/e* 136 ⟶ 68 and *m/e* 136 ⟶ 108 for compound (I) were not observed, although a weak metastable peak corresponding to the 136 ⟶ 68 transition was observed in compounds (II) and (III).

One of the results of electron impact on compounds (I)—(III) is cleavage of the cyclobutane ring. Dependent upon which way the ring is split, either an ion of *m/e* 108 and an ethylene molecule or an ion of *m/e* 68 and an isoprene molecule are formed. Further fragmentation of the ion *m/e* 68 gives a spectrum similar to that of

TABLE 1

Mass spectra

Relative intensity (*m/e* 68 = 100)

m/e	(I)	(II)	(III)	(IV)	(V)
26	3				2
27	19	11	8	10	13
28	12	4	2		27
29	6	3	3	5	7
32	1				6
38	4	1			1
39	25	15	14	12	20
40	14	9	8	5	8
41	23	16	15	15	21
42	7	5	6	3	4
43	1	2	1	2	5
44					5
50		1	1	1	3
51	7	4	3	4	5
52	4	2	2	3	4
53	32	22	19	15	19
54	2	1	1	2	3
55	7	4	3	11	8
63	2	1	1	1	3
65	6	3	4	5	6
66	4	4	3	3	4
67	53	55	47	35	35
68	100	100	100	100	100
69	7	7	8	8	7
77	9	5	7	8	13
78	2	1	1	4	4
79	10	9	8	14	22
80	6	5	6	7	11
81	8	8	8	10	13
82	1	2	1	3	2
91	7	10	7	9	14
92	5	8	13	9	21
93	28	34	43	29	65
94	11	13	12	14	20
95	5	4	3	7	8
105	2	2	2	4	4
106				3	1
107	18	13	13	22	18
108	12	4	4	8	6
109	1			2	
119				3	2
121	13	13	8	15	19
122	1	1		2	2
136	6	3	1	17	27
137				3	3

[1] J. H. Beynon, 'Mass Spectrometry and its Applications to Organic Chemistry,' Elsevier, Amsterdam, 1960.

[2] Mass Spectral Data Sheet No. 242, American Petroleum Institute Research Project 44.

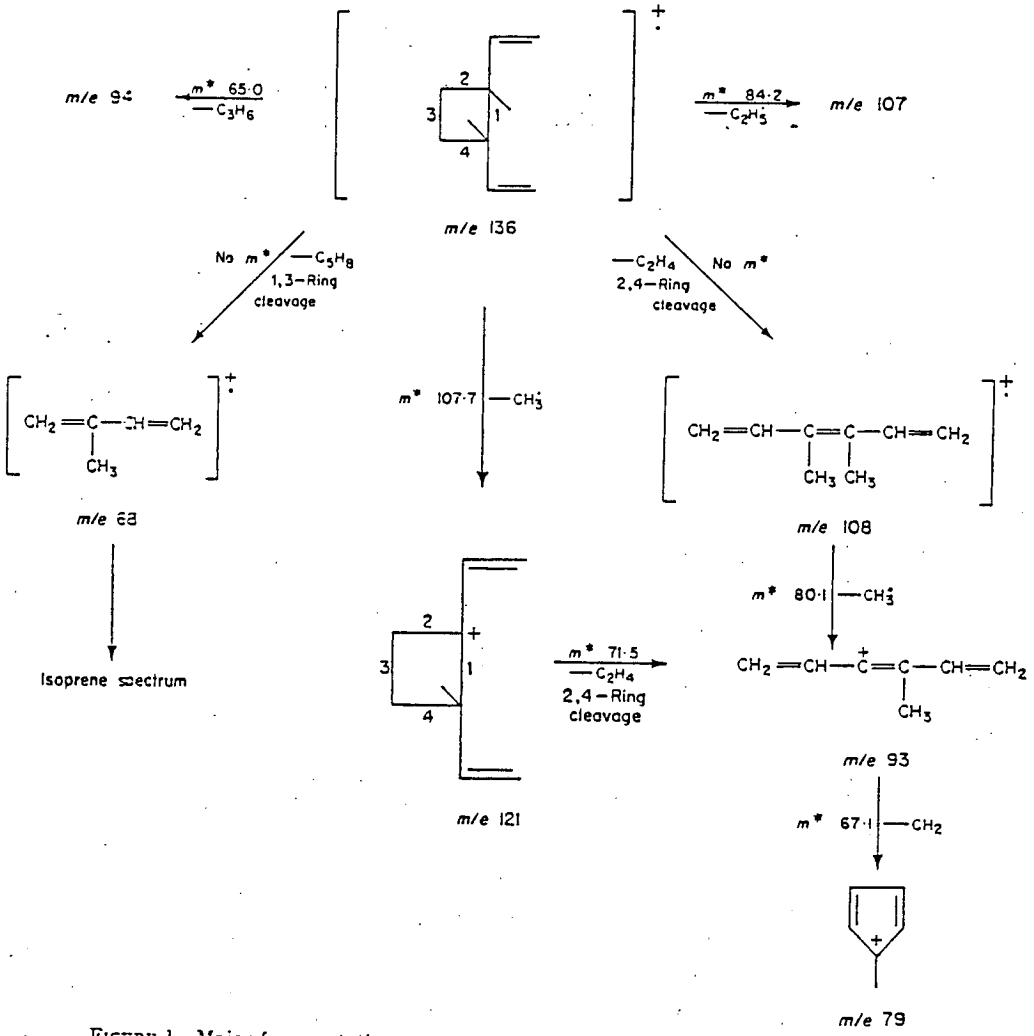


FIGURE 1 Major fragmentation routes of *trans*-1,2-dimethyl-1,2-divinylcyclobutane

isoprene while the further fragmentations of the ion of *m/e* 108 result in the production of ions of *m/e* 93 and 79. The lack of a metastable ion corresponding to the transition *m/e* 136 ⟶ 68 in compound (I) is surprising since the corresponding metastable ions are observed in compounds (II) and (III) although they are of low intensity. The possibility that the absence of the metastable ion could be explained by the thermal decomposition of the parent compound to isoprene can be discounted since the intensity of the peak for ion *m/e* 68 expressed as a percentage of the total ion intensity ($100I/\Sigma I$) did not change significantly as the temperature of the source block was varied over the range 60—180°. Furthermore, the appearance potential of the ion *m/e* 68 differs significantly from that of isoprene, as the ionisation efficiency curves in Figure 2 show. The appearance potentials obtained were 8·7 ± 0·1 ev for isoprene and 9·4 ± 0·1 ev for the ion *m/e* 68 from the dimer.

It is significant that the metastable ions corresponding to the transition *m/e* 136 ⟶ 68 in (II) and (III) are very weak and that in (I)—(III) no metastables corresponding to the transition *m/e* 136 ⟶ 108 occurred.

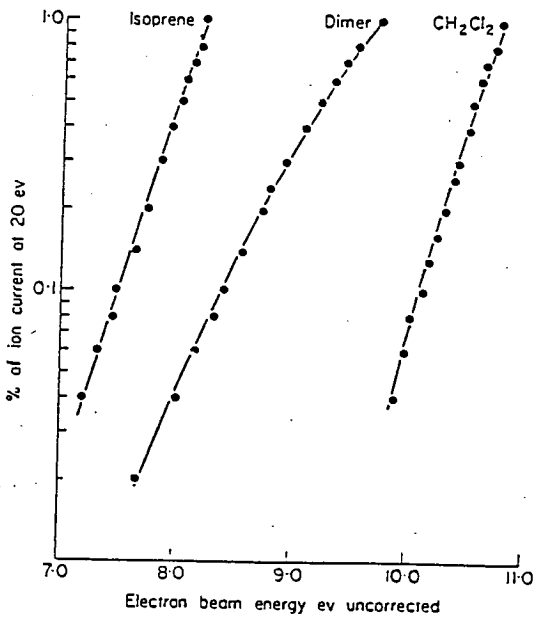


FIGURE 2 Ionisation efficiency curves

This suggests that processes involving cleavage of the ring in the molecular ion are rapid.

Another important pathway for degradation of the molecular ion of the cyclobutane derivatives is the loss of a methyl radical to give an ion of *m/e* 121. The positive charge on this ion will either be localised on the cyclobutane ring in (I) or on the side chain in (III). Subsequent cleavage of the cyclobutane ring in the ion *m/e* 121 results in the production of an ion of *m/e* 93 and a molecule of ethylene. Loss of a CH_2 fragment from the ion of *m/e* 93 results in an ion of *m/e* 79. It is interesting to note that ring cleavage in the fragment ion *m/e* 121 leads to a metastable ion in compounds (I)—(III) whereas the metastable ion corresponding to ring cleavage in the molecular ion was not observed.

The modes of fragmentation of the parent ion of the cyclobutane derivatives which lead to the production of ions of *m/e* 107 and 94 are difficult to interpret. The formation of these ions must be accompanied by the production of an ethyl radical and a molecule of propene respectively. Subsequent fragmentation of ions *m/e* 107 and 94 involves loss of a molecule of ethylene which

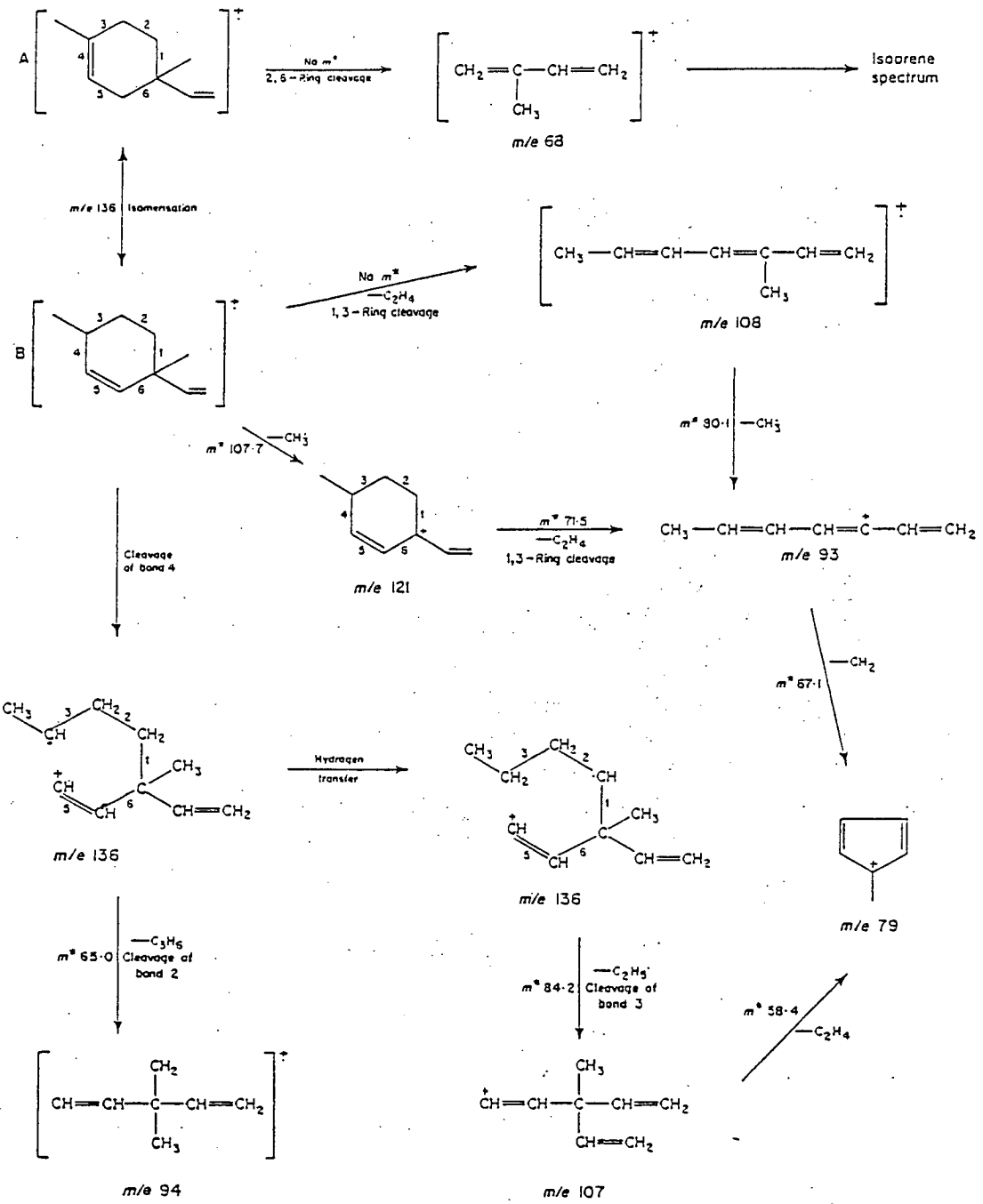


FIGURE 3 Major fragmentation routes of 1,4-dimethyl-4-vinylcyclohexene

is most readily interpreted as arising from cleavage of the ring in the ions.

Mass Spectra of Cyclohexene Derivatives.—Figure 3 shows the possible fragmentation pathways of compound (IV) which lead to ions having *m/e* values greater than or equal to *m/e* 68 and which have the same *m/e* value as those from the cyclobutanes (Figure 1). The fragmentation processes in compound (V) are the same as in compound (IV) except that, as in the cyclobutanes, the position of the methyl groups and charge sites differ in the molecular and fragment ions of the isomers. The metastable ions corresponding to the fragmentation processes for compound (V) are the same as for compound (IV). No metastable ion corresponding to the transition *m/e* 136 ⟶ 108 was observed in either compound.

The observation that fragmentation of derivatives of cyclohexene involves isomerisation and hydrogen transfer processes [3] suggests that the fragmentation in compound (IV) results from the breakdown of isomers A and B (see Figure 3).

Fragmentation of the rings in isomers A and B by a retro-Diels–Alder process [4] leads, *via* 2,6-bond fission in isomer A, to the ion *m/e* 68 and, *via* 1,3-bond fission in isomer B, to the ion *m/e* 108.

The formation of the other main ions of *m/e* > 68 is readily explained in terms of fragmentation of isomer B. The ion of *m/e* 107 results from cleavage of bond 4 in the ring of the molecular ion followed by migration of a hydrogen atom and subsequent cleavage of bond 3. This ion is further fragmented as shown in Figure 3. The formation of the ion *m/e* 94 arises by cleavage of bond 2 in the molecular ion as shown in Figure 3.

Loss of a methyl radical from isomer B results in an ion of *m/e* 121. Cleavage of the ring in this ion yields an ion of *m/e* 93 and a molecule of ethylene. As in the case of the cyclobutane systems, the metastable ion corresponding to the transition involving ring cleavage of the ion *m/e* 121 is observed.

The ion of *m/e* 93 can also be formed by loss of a methyl radical from the ion of *m/e* 108. A CH_2 fragment can be split from the ion of *m/e* 93 with the resultant formation of an ion *m/e* 79. This latter ion can also be formed by loss of an ethylene molecule from the ion of *m/e* 107.

It is noteworthy that, as in the case of the cyclobutane derivatives, no metastable ion could be observed for the fragmentation involving the split of an ethylene molecule from the ring of the molecular ion.

Values of $100I/\Sigma I$.—The peak intensities of the ions shown in Figures 1 and 3 are listed in Table 2 as percentages of the sum of all peak intensities ($100I/\Sigma I$).

Since the value of $100I/\Sigma I$ for a molecular ion is a measure of the stability of that ion [5] the results shown in Table 2 for the ion of *m/e* 136 indicate the relative stabilities of the molecular ions formed from compounds (I)—(V). The molecular ions formed from the cyclobutane derivatives are less stable than those formed from the cyclohexene derivatives and the order of stabilities within these groups is (I) > (II) > (III) and (V) > (IV).

TABLE 2

Values of $100I/\Sigma I$ for major ions from compounds (I)—(V)

m/e	(I)	(II)	(III)	(IV)	(V)
136	1·16	0·73	0·37	3·76	4·35
121	2·61	3·22	2·06	3·31	3·02
108	2·32	1·04	1·01	1·75	1·01
107	3·63	3·01	3·32	4·70	2·95
94	2·18	3·11	2·97	3·01	3·20
93	5·72	8·30	10·82	6·39	10·52
79	2·00	2·08	1·88	3·01	3·54
68	20·17	24·09	25·13	21·83	16·24

The base peak in all the spectra corresponds to the molecular ion of isoprene. Since this ion is common to compounds (I)—(V) the difference in the $100I/\Sigma I$ values must arise from differences in the stabilities of the molecular ions which are the precursors of the isoprene ion. As the stabilities of the molecular ions of compounds (I), (II), and (III) are in the order (I) > (II) > (III), the values of $100I/\Sigma I$ for the ion of *m/e* 68 are in the expected order. Similarly the order of the values of $100I/\Sigma I$ for the ion *m/e* 68 from compounds (IV) and (V) is as expected.

Although the values of $100I/\Sigma I$ for the ions other than *m/e* 136 and 68 vary between compounds (I)—(V), these values cannot be used to predict the relative stabilities of the ions since they are dependent upon the stabilities of both the parent and daughter ions. However, the values of $100I/\Sigma I$ given in Table 2 are of use in characterising compounds (I)—(V).

EXPERIMENTAL

Mass spectra were recorded at the N.P.L. on an AEI MS 9 instrument. The electron beam energy was 70 ev and the temperature of the gas inlet system was 100°. Ionisation efficiency curves were obtained by an automatic voltage scanning device [6] using a trap current of 20 μA and zero repeller voltage. Appearance potentials were evaluated by the extrapolated voltage difference method and the reference ion was the molecular ion of dichloromethane (*m/e* 84, I.P. 11·4 ± 0·1 ev).[7] Metastable peaks were allocated using an Elliot 4120 computer. All mass spectra have been submitted to the Mass Spectrometry Data Centre, Aldermaston.

Compounds (I)—(V) were prepared by the photodimerisation of isoprene.[8] The compounds were purified by g.l.c. and characterised by i.r. and n.m.r. spectroscopy and by measurement of refractive index.

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Molecular Complexes

Dr CHJ Wells

Molecular complexes resulting from the physical interactions of molecules are a widespread chemical phenomenon. Their formation can influence reaction pathways and may be detected spectroscopically.

Many molecules which are not capable of reacting 'chemically' often interact 'physically' and are bound together in the form of a molecular complex by weak forces of coordination. Such molecular complexes are generally formed as a result of interaction between 'electron rich' sites in a donor molecule and 'electron deficient' sites in an acceptor molecule. The binding between the components of a complex is generally weak and in solution a dynamic equilibrium exists between the complex and components:

$$\text{Donor} + \text{Acceptor} \rightleftharpoons \text{Molecular complex}$$

Since a wide variety of molecular types is capable of interaction, molecular complexes are widespread in chemistry, and since the formation of a molecular complex between reactive species may exert an influence on the reaction pathway, it is important that the possibility of the existence of complexes be recognized.

Types of donor and acceptor

Donor and acceptor molecules can be classified according to the nature of the orbitals in which the electrons involved in the interaction are located. On this basis there are two types of donor, *viz*: π-donors and n-donors. Aromatic hydrocarbons provide an example of π-donors: the π-electron system of the hydrocarbon acts as the donor site when complexes are formed. Compounds containing heteroatoms are often n-donors and in these the electrons available for sharing are located in the non-bonding orbitals (n-orbitals) associated with the heteroatom.

Acceptor molecules can be divided into π-acceptor types and σ-acceptor types, although it should be recognized that many acceptors do not fall into either class. Picrates are molecular complexes in which the acceptor species, picric acid, is of the π-type. Since aromatic hydrocarbons are π-donors the picrates formed with such donors are referred to as π,π complexes. Another type of complex involving π-acceptors is that formed between an amide and an aromatic hydrocarbon. In these, the amides act as n-donors by using the lone-pair electrons on the oxygen atom while the aromatic hydrocarbons act as π-acceptors by virtue of the π-orbitals of the ring system. Such complexes are termed n,π complexes.

In the complexes formed between carbonyl compounds and halogens the interaction between donor and acceptor involves the non-bonding orbital on the oxygen atom and a σ-orbital of the halogen ($R_2C{=}O\cdots X{-}X$). A complex of this type is termed a n,σ complex. Complexes in which a hydrogen bond exists between the donor and acceptor species are an important class of n,σ complex. The hydrogen-bonded complexes formed between carbonyl compounds as donors and alcohols as acceptors are typical examples:

$$R_2C{=}O + H{-}O{-}R \rightleftharpoons R_2C{=}O\cdots H{-}O{-}R$$

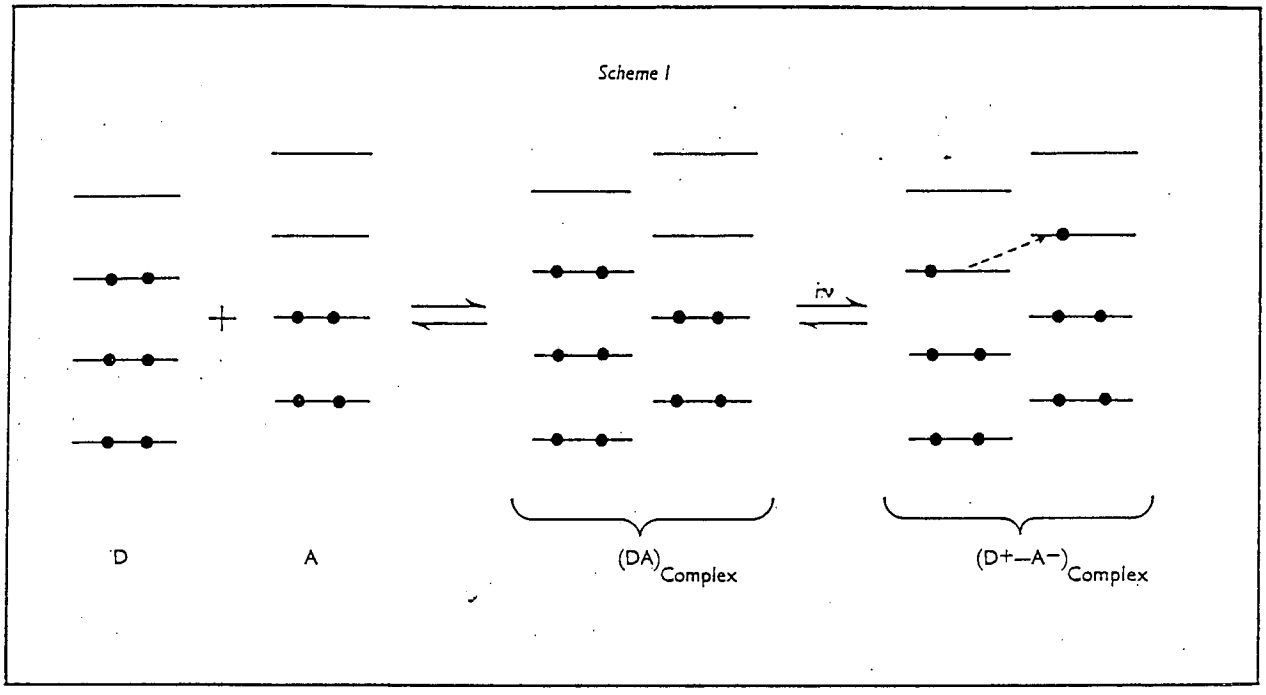
Hydrogen bonding can also occur between π-type donors and σ-type acceptors as exemplified by the benzene–chloroform complex (π,σ complex).

$$C_6H_6 + H{-}CCl_3 \rightleftharpoons C_6H_6\cdots H{-}CCl_3$$

Some examples of compounds belonging to the different donor and acceptor classes are given in Table 1. Although complexes arising from the four possible types of interaction ($\pi \longleftrightarrow \pi$, n $\longleftrightarrow \pi$, $\pi \longleftrightarrow \sigma$, n $\longleftrightarrow \sigma$) have been characterized it does not follow that a donor molecule of either the π- or n-type will automatically

Table 1. Types of donor and acceptor

Donors	Acceptors
π-type	π-type
Aromatic hydrocarbons	Aromatic hydrocarbons and alkenes with electronegative substituents
Alkenes	Anhydrides
	Quinones
n-type	σ-type
Alcohols	Metal halides
Organic sulphides	Halogens
Ethers	Salts of Ag, Cu(I), Hg(II)
Heterocycles	Hydrogen donors, *e.g.* alcohols, hydrogen halides, haloforms



form a complex with any acceptor of the π- or σ-type since other factors, such as the extent of orbital overlap between potential donors and acceptors, can determine whether or not complexes are formed.

Electronic transitions in molecular complexes

Many molecular complexes, such as the picrates, are intensely coloured and it is now commonly accepted that the colour of these complexes is associated with the transfer of an electron from a molecular orbital of the donor to a molecular orbital of the acceptor. The lowest energy transition in the complex will correspond to the promotion of an electron from the highest occupied molecular orbital (HOMO) of the donor D to the lowest vacant molecular orbital (LVMO) of the acceptor A (*Scheme I*). Since the absorption of radiation brings about the transfer of an electron from the donor to acceptor species, the process is often termed a 'charge-transfer' transition.

The energy required for the promotion of an electron from the HOMO of the donor to the LVMO of the acceptor will obviously vary for different donor–acceptor pairs and although the energy difference is often such that the molecular complexes absorb visible radiation and are coloured, it is also frequently the case that the energy required for the transition corresponds to energy in the ultraviolet range and the complexes are colourless.

In the above model, the energy ΔE required for the promotion of an electron is given by the expression

$$\Delta E = E_{A(LVMO)} - E_{D(HOMO)} \quad (1)$$

where the E terms represent the energies of the appropriate orbitals of the acceptor and donor. If the energies of the orbitals are expressed in terms of the Hückel molecular orbital parameters α and β and the orbital coefficients χ, then equation 1 can be written as

$$\Delta E = (\alpha - \chi_A\beta) - (\alpha + \chi_D\beta) \quad (2)$$

$$= -\chi_A\beta - \chi_D\beta \quad (3)$$

For a series of complexes of different donors with the same acceptor, equation 3 can be reduced to

$$\Delta E = \text{constant} - \chi_D\beta \quad (4)$$

The validity of equation 4, and hence the validity of the charge-transfer model, for representing the electronic transition of lowest energy in molecular complexes has been verified. A straight line is obtained when the experimentally derived values of ΔE for the complexes formed between aromatic hydrocarbons as donor and tetracyanoethylene as acceptor are plotted against the coefficients χ_D for the hydrocarbons.[1]

Wave-mechanical description

Mulliken[2] has proposed that a molecular complex formed by the interaction of a donor molecule D and an acceptor molecule A is a resonance hybrid of two structures—one a no-bond structure (D,A) in which the two molecular species are bound by van der Waal's forces, and the other an ionic structure (D^+—A^-) in which an electron is transferred from the donor molecule D to the acceptor molecule A with the formation of a covalent bond between the donor and acceptor. Mulliken expressed the wave function ψ_N of the ground state of the complex by the equation

$$\psi_N = a\psi_0(D,A) + b\psi_1(D^+—A^-) \quad (5)$$

where a and b are constants. The terms $a\psi_0(D,A)$ and $b\psi_1(D^+—A^-)$ represent respectively the contributions to the ground state of the no-bond structure and

the ionic structure. The energy of the ionic structure was considered to be higher than that of the no-bond structure and the contribution of the former structure to the wavefunction of the ground state was considered to be low (*i.e.* $a \gg b$). In the benzene–iodine complex, for instance, the contribution of the ionic state is of the order of 8 per cent.

The absorption of ultraviolet or visible radiation by a complex corresponds to the transfer of an electron from the donor to acceptor, and the resulting excited state is largely ionic in character. The wavefunction ψ_E for the complex in the excited state is given by the equation

$$\psi_E = a^*\psi_1(D^+—A^-) - b^*\psi_0(D,A) \quad (6)$$

where $a^* \approx a$, $b^* \approx b$ and $a^* \gg b^*$. The term $a^*\psi_1(D^+—A^-)$, representing the contribution of the ionic structure to the excited state, is of greater magnitude than the term $b^*\psi_0(D,A)$ which represents the contribution of the no-bond structure.

Ionic character of complexes

According to Mulliken's concept of molecular complexes[2] the contribution of the ionic structure $D^+—A^-$ to the ground state of the complex is generally small and it is the no-bond (D,A) form which provides the main contribution. Measurement of the dipole moments of complexes and of their components can often lead to values for the coefficients a and b in equation 5, and thus to values for the percentage ionic character ($100b^2/a^2 + b^2$) of the complexes in the ground state.[3] Table 2 lists values for the percentage ionic character of the ground state of selected complexes. This can vary greatly from complex to complex. The π,π complexes formed between aromatic hydrocarbons as donors and *s*-trinitrobenzene and tetracyanoethylene as acceptors possess very little ionic character whereas the n,π complexes formed between aliphatic and aromatic amines as donors and picric acid as acceptor are significantly ionic.

The majority of complexes which have been investigated are essentially non-ionic and as would be expected for complexes which are formed with minimum perturbation of the components, the properties of these complexes are not, in general, significantly different from those of the components. However, complexes in which the structure $D^+—A^-$ is dominant often exhibit properties which are markedly different from those of the components.

Table 2. Ionic character of complexes in the ground state

Complex	Solvent	Percentage ionic character
Benzene–iodine	Cyclohexane	8.2
Triethylamine–iodine	Dioxane	59.0
Naphthalene–*s*-trinitrobenzene	Carbon tetrachloride	2.8
Naphthalene–chloranil	Carbon tetrachloride	4.1
Hexamethylbenzene–tetracyanoethylene	Carbon tetrachloride	6.7
Aniline–picric acid	Dioxane	33.1
Ethylamine–picric acid	Dioxane	64.0

In the ionic form of a complex, the unpaired electrons occupying the HOMO and LVMO orbitals of the donor and acceptor respectively can either have their spins anti-parallel in which case the complex is a singlet state and diamagnetic, or they can have their spins parallel in which case the complex is a triplet state and is paramagnetic. If the complex is sufficiently ionic in character then the paramagnetic triplet state may not be of much greater energy than the ground state and the complex will be measurably paramagnetic at room temperature.

One method of determining whether or not a complex is paramagnetic is by means of electron spin resonance (esr) spectroscopy. A paramagnetic complex should exhibit an esr signal and under favourable conditions the esr spectra of the D^+ and A^- radical ions may be picked out from the spectrum, *e.g.* the esr spectrum of the solid adduct formed between *N,N,N',N'*-tetramethylphenylenediamine as donor and *p*-chloranil as acceptor exhibits lines from both the donor and acceptor radical ions.[4]

Detection of complexes

When a donor and acceptor species are mixed in solution the ultraviolet-visible absorption spectrum of the mixture often exhibits bands which are not present in the spectra of the individual species. These new absorption bands could be caused by an electronic transition associated either with a molecular complex or with some reaction product. In order to ascertain whether or not the absorption bands arise from a molecular complex use is made of the Benesi–Hildebrand equation[5] which relates the absorbance of a 1:1 molecular complex to the concentration of the component species. If any new absorption band is due to the presence of a molecular complex then a plot of the reciprocal of the absorbance at a particular wavelength against the reciprocal of the donor concentration at a constant concentration of acceptor should yield a straight line.

The Benesi–Hildebrand equation has the disadvantage that it can only strictly be applied to complexes with 1:1 stoicheiometry. An alternative method of ascertaining whether or not a particular absorption band is due to a molecular complex is Job's method of continuous variation.[6] This involves making up mixtures containing different ratios of the components and plotting the absorbance of each mixture, at a particular wavelength, against the mole ratio of one of the components in the mixture. If the absorption band is the result of a charge-transfer transition in a complex then a smooth plot will be obtained with a maximum corresponding to the stoicheiometric composition of the complex. A plot is illustrated in *Fig. 1* for the 1:1 complex formed between hexamethylbenzene and tetracyanoethylene.

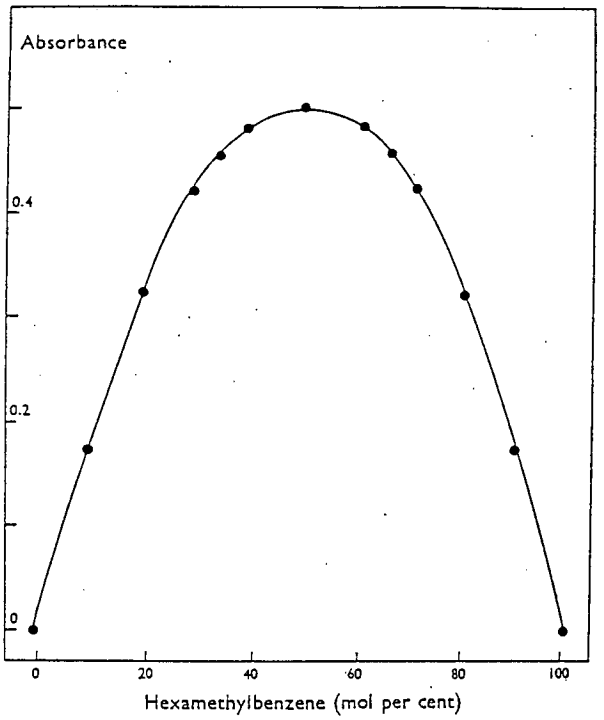


Fig. 1. Job plot for hexamethylbenzene–tetracyanoethylene complexes.[7]

In many cases the absorption bands of molecular complexes in the ultraviolet and visible regions cannot be observed because of masking by the absorption bands of the components, and other methods have to be used to detect the presence of complexes. Methods based on the change in physical properties of a system as the composition of the component mixture is changed are commonly used to establish both the existence of a complex and also the ratio of the components in the complex. For example, Reeves and Schneider[8] used freezing-point–composition diagrams to study complex formation between alkenes and chloroform, and from diagrams such as the one shown in *Fig. 2* they were able to determine the stoicheiometry of any complexes formed. The plot shows that a 2:1 chloroform–hex-1-ene complex is formed between these components.

The differences between the infrared spectra of molecular complexes and those of the individual components are often sufficiently great to enable the presence of molecular complexes in a system to be detected, although the differences depend upon the type of complex formed. For π,π complexes formed between aromatic hydrocarbons and *s*-trinitrobenzene the interaction is largely delocalized, and the infrared spectra of the solid complexes are essentially composites of those of the free components with only minor changes in the intensities and positions of the bands. On the other hand, in the n,σ complexes formed between aromatic carbonyl compounds and halogens the interaction is localized between the

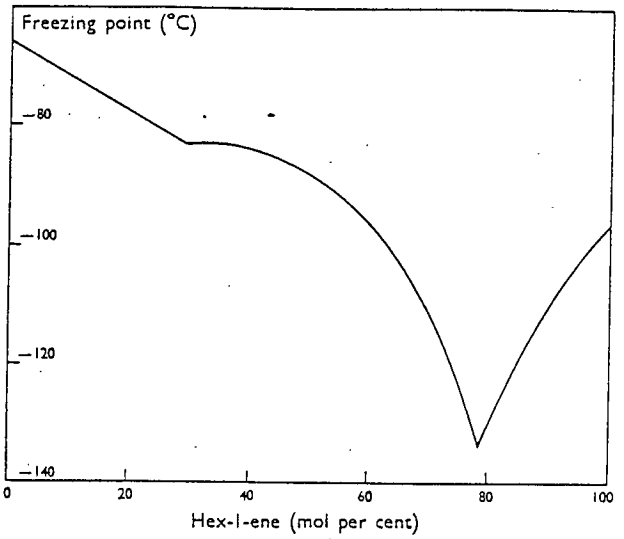


Fig. 2. Freezing-point–composition diagram for chloroform–hex-1-ene system.

oxygen atom of the carbonyl group and one of the atoms of the halogen ($R_2C{=}O\cdots X{-}X$), and here significant changes occur in the positions of the bands associated with the site involved in the interaction. Similarly, in hydrogen-bonded complexes involving the O—H grouping, the position of the band representing the O—H stretching vibration in the complex is often markedly different from the position in the non-bonded component.

Nuclear magnetic resonance (nmr) spectroscopy can also be used to detect the existence of complexes in solution. As for infrared spectroscopy, the spectra of the complexes are generally composites of the spectra of the individual components, although the resonance positions of nuclei often change when complexed. For example, the resonances observed in the nmr spectrum of a solution of dimethylformamide in a non-complexing solvent such as cyclohexane or in a complexing solvent such as benzene, correspond to those expected for the individual components, although the resonance positions of the methyl protons in dimethylformamide are different in the two solvents.[9] This difference arises because in the molecular complex formed between dimethylformamide and benzene the magnetic environments and hence the resonance positions of the methyl protons differ from those in the 'free' dimethylformamide.

Mass spectrometry is a technique which can sometimes be applied to the identification of non-ionic solid complexes. Since the binding energy between donor–acceptor components in solid complexes is relatively low (4–40 kJ mol^{-1}), complexes will dissociate into component species on electron impact in the spectrometer, and in such cases the spectrum recorded would be equivalent to the sum of the spectra of the

(concluded on page 183)

Molecular Complexes

(concluded from page 178)

components. Alternatively, if one of the components is markedly more volatile than the other, then the spectrum recorded may correspond to that of the more volatile species. Thus, comparison of the spectrum of any solid product isolated from a mixture of donor and acceptor species, with the spectra of the donor and acceptor will reveal whether or not the product is a molecular complex.

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THE NATURE OF THE PHOTOREACTIVE TRIPLET STATE OF 9-ANTHRALDEHYDE

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The photoreduction of aromatic ketones normally occurs via the intermediacy of an n, π^* triplet state (1) although in certain cases the reduction can proceed via a π, π^* triplet state (2). The photoreactive triplet state may not necessarily be the lowest energy state of the triplet manifold. In the case of 9-anthraldehyde the triplet sate of lowest energy is π, π^* in character (3) and non-reactive with respect to photoreduction (4), and it has been deduced (4) that the higher energy photoreactive state is n, π^* in character. 9-anthraldehyde is photoreduced in the presence of toluenes (4), and the results given below for comparative reductions in toluenes provide further evidence that the photoreactive state is n, π^* in character.

Comparative experiments were performed by irradiating at 366nm sealed, degassed solutions of 9-anthraldehyde (0.01M) and toluene or substituted toluene (0.1 - 0.5M) in benzene. The photolysis were carried out in an apparatus previously described (5) and the quantum yields for the photoreduction of 9-anthraldehyde by toluene, Φ_o, and by substituted toluenes, Φ, were calculated after allowance had been made for the consumption of 9-anthraldehyde by photo-dimerisation and for the different numbers of ' reactive ' protons in the toluenes used. The plot of $\log_{10} \Phi/\Phi_o$ against the Hammett σ^+ constants for the substituents is shown in Fig. 1.

The value for the reaction constant ρ^+ derived from the straight line plot is -1.31. This value is to be compared with the corresponding value of -1.16 for the photoreactive triplet state of benzophenone (6). Since it has been well established that the photoreactive triplet state of benzophenone is n, π^* in character, the similarity between two values indicates that the reactive triplet state of 9-anthraldehyde is also n, π^* in character.

It is to be expected that the n, π^* triplet states of 9-anthraldehyde and benzophenone would have similar electronegativities, and hence the slightly larger negative value of σ^+ for the triplet state of 9-anthraldehyde may reflect a decreased reactivity of this triplet state as compared to that of benzophenone. This would be in accord with the lower energy (58 - 64 Kcal/mole) of the triplet state of anthraldehyde (4) compared to the higher energy (69 Kcal/mole) of the triplet state of benzophenone (7).

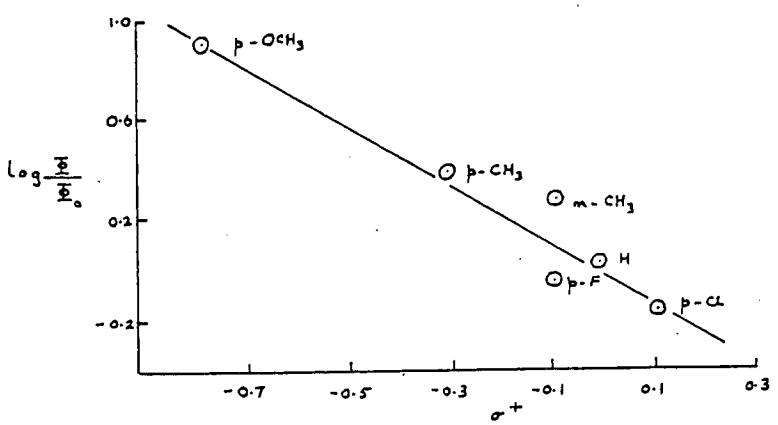

Fig. 1. Relationship between relative reactivities of toluenes and Hammett σ^+ constants.

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Mass Spectra of Isomers. Part II.[1] Electron-impact-induced Isomerisation of Some Derivatives of Cyclobutane

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Mass Spectra of Isomers. Part II.[1] Electron-impact-induced Isomerisation of Some Derivatives of Cyclobutane

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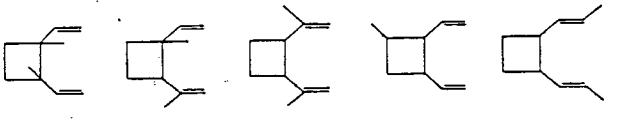
The electron-impact-induced fragmentation of some isomeric derivatives of cyclobutane is interpreted in terms of the formation of a cyclohexene intermediate; the structure of the intermediate is dependent upon the parent cyclobutane. The losses of $C_2H_5^{\bullet}$ and C_3H_6 from the molecular ions are a consequence of the formation of the cyclohexene intermediates.

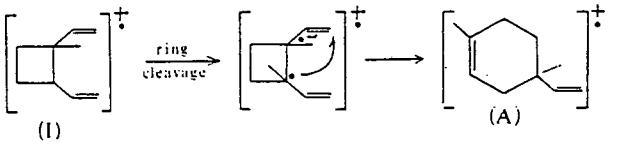
It is well known that the mass spectra of isomers are essentially similar and in the case of isomeric trimethylcyclopentadienes, for example, the similarity between the spectra has been interpreted [2] as resulting from the formation of a common cyclic benzenium species prior to fragmentation. An indication of a change in structure of the molecular ion prior to fragmentation is the presence of ions the formation of which cannot be readily explained on the basis of the original structure. In the case of isomeric derivatives of cyclobutane [(I)—(III)] the presence in the spectra of ions which correspond to losses of $C_2H_5^{\bullet}$ and C_3H_6 from the molecular ions could not be accounted for in terms of fragmentation of the cyclobutane system.[1] In order to ascertain whether these losses were a consequence of the formation of an intermediate molecular ion, of different structure from the parent molecular ion, two further isomeric cyclobutanes [(IV) and (V)] have been prepared. Their mass spectra (Table 1) are similar to those of compounds (I)—(III) [1] and show the same metastable transitions (m/e 136 ⟶ 107, m^* 84·2; m/e 136 ⟶ 94, m^* 65·0), corresponding to the loss of $C_2H_5^{\bullet}$ and C_3H_6 from the molecular ions.

The fragmentations m/e 136 ⟶ 107 and 136 ⟶ 94 also occur in isomeric cyclohexene derivatives and a mechanism for the fragmentations has been proposed previously.[1] The formation of the ions of m/e 107 and



(I) (II) (III) (IV) (V)

94 from the molecular ions of the cyclobutanes is now explained by a mechanism which involves isomerisation to a cyclohexene derivative and subsequent fragmentation as previously described. The mechanism for the isomerisation involves a six-membered transition state, as shown for the isomerisation of compound (I) to the corresponding cyclohexene (A).



(I) (A)

Since the proposed isomerisation involves free-radical

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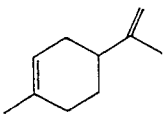
TABLE 1

Mass spectra of compounds (IV) and (V) [mass spectra of compounds (I), (II), and (III) have already been reported [1]]

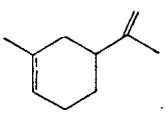
Relative intensity (*m/e* 68 ≡ 100) (electron-beam energy 70 ev)

m/e	(IV)	(V)	*m/e*	(IV)	(V)
27	6	5	69	7	5
28	2	3	77	5	3
29	2	2	78	1	1
39	11	9	79	12	3
40	5	5	80	3	1
41	11	9	81	2	2
42	3	3	91	3	3
51	2	2	92	2	2
52	2	1	93	8	8
53	11	10	94	4	4
55	3	2	95	2	1
65	3	3	107	2	2
66	3	2	121	2	1
67	32	32	136	1	4
68	100	100			

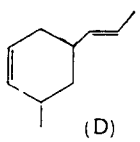
addition to an olefinic system, it is expected that if there are alternative sites for addition then the addition will occur preferentially at the site of lowest electron density. Thus the isomerisation of compounds (II) and (IV) will proceed *via* free-radical addition to the ethylenic group in each compound, rather than *via* free-radical addition either to the isopropenyl group in compound (II) or to the propenyl group in compound (IV). The isomerisation of compounds (II) and (IV) will result in the formation of the cyclohexenes (B) and (D) respectively, whereas the isomerisation of compounds (III) and (V) will form the cyclohexenes (C) and (E) respectively.



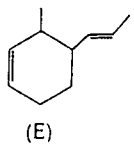
(B)



(C)



(D)



(E)

The fragmentation of the molecular ions of species (A) and (B) has been discussed previously [1] when it was shown that the ions of *m/e* 107 and 94 were formed by a process which involved migration of the double bond in the ring followed by ring cleavage and then, either subsequent cleavage of the chain with loss of a C_3H_6 molecule, or hydrogen transfer and chain cleavage with loss of a $C_2H_5^{\bullet}$ radical. The formation of ions of *m/e* 107 and 94 from species (C), (D), and (E) can also be accounted for in this way, although no migration of the double bond before ring cleavage is necessary in species (D).

The mass spectra of compounds (I)—(V) all show that the same fragment ions are formed in each case, although there are significant differences in the values of $100I/\Sigma I$ for some of the ions. The values of $100I/\Sigma I$ for the ions of *m/e* 136, 107, 94, and 68 formed in the fragmentation of compounds (I)—(V) at an electron-beam energy of 70 ev are given in Table 2. It can be

TABLE 2

Values of $100I/\Sigma I$ for molecular and fragment ions (70 ev)

Cyclobutane	(I)	(II)	(III)	(IV)	(V)
Cyclohexene intermediate	(A)	(B)	(C)	(D)	(E)
(*m/e*)					
(136)	1·16	0·73	0·37	0·41	1·53
(107)	3·63	3·01	3·32	0·89	0·88
(94)	2·18	3·11	2·97	1·70	1·80
(68)	20·17	24·09	25·13	38·39	41·95

seen that the values for the fragment ions are similar for compounds (II) and (III), and for compounds (IV) and (V), and that these values are different from those for the ions from compound (I). It is significant in this respect that whereas the isomerisation of compounds (II) and (III) yields isopropenyl-substituted cyclohexenes, and the isomerisation of compounds (IV) and (V) yields propenyl-substituted cyclohexenes, the isomerisation of compound (I) yields a vinyl-substituted cyclohexene. Thus the values of $100I/\Sigma I$ for the fragment ions apparently depend upon which of the three types of cyclohexene intermediate is formed on isomerisation of the parent molecular ion. The values of $100I/\Sigma I$ at an electron beam energy of 20 ev for the ions of *m/e* 107, 94, and 68 formed from each type of cyclohexene intermediate are shown in Table 3. Comparison of the values given in Tables 2 and 3 reveals

TABLE 3

Values of $100I/\Sigma I$ for molecular and fragment ions (20 ev)

Cyclobutane	(I)	(II)	(III)	(IV)	(V)
Cyclohexene intermediate	(A)	(B)	(C)	(D)	(E)
(*m/e*)					
(136)	1·39	1·68	1·03	0·62	1·88
(107)	4·32	5·02	5·17	1·57	1·78
(94)	2·62	5·52	5·00	2·86	3·05
(68)	26·81	31·59	32·53	59·91	54·86

that for each type of cyclohexene intermediate, the values of $100I/\Sigma I$ for the fragment ions increase when the electron beam energy is decreased from 70 to 20 ev. This may be taken as evidence that the ions of *m/e* 107, 94, and 68 are primary fragment ions formed directly from the corresponding molecular ion.

Compounds (I)—(III) are dimers of isoprene and compounds (IV)—(V) are dimers of penta-1,3-diene and thus the fragmentation *m/e* 136 ⟶ 68 in each case involves breakdown of the molecular ion of the dimer to that of the monomer. The values of $100I/\Sigma I$ for the ion of *m/e* 68 from the pentadiene dimers (IV) and (V) are much higher than the values for the isoprene dimers (I), (II), and (III). This is a consequence of the higher stability of the unbranched pentadiene chain compared with that of the branched isoprene chain. Further,

on the basis of the localised charge site concept, the ion of *m/e* 68 from compound (I) may be expected to be least stable because of the methyl branch at the charge site. The ions of *m/e* 68 from compounds (II) and (III) will be of intermediate stability, since the charge site may or may not carry a methyl group depending upon which half of the fragmented dimer carries the charge.

EXPERIMENTAL

Mass spectra were recorded at the National Physical Laboratory on an AEI MS 9 instrument, at electron-beam energies of 70 and 20 ev. The temperature of the gas inlet system was 100°. Metastable peaks were allocated by computer.

Compounds (I)—(III) were prepared by the photodimerisation of isoprene and compounds (IV)—(V) by the photodimerisation of penta-1,3-diene.[3] The compounds were purified by preparative gas-phase chromatography and characterised by i.r. and n.m.r. spectroscopy.

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Electron Spin Resonance of the Triplet State of Some Aromatic Carbonyl Compounds

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Summary The e.s.r. spectra of some carbonyl derivatives of naphthalene which possess lowest triplet states of the π,π^* type, exhibit triplet state signals from which the zero-field-splitting parameters D and E can be calculated.

THE lowest triplet state of aromatic carbonyl compounds can be either n, π^* or π,π^* in character, or in certain cases, charge-transfer in character.[1,2] The majority of aromatic carbonyls possess lowest triplet states of the n,π^* type, and the e.s.r. spectra of the triplet state of these compounds have not been observed on account of the short phosphorescence lifetimes ($<0{\cdot}1$ sec.) of these states. Studies related to the photochemistry of aromatic carbonyl compounds have revealed that a number of aromatic carbonyl compounds possess lowest triplet states of the π,π^* type and that the phosphorescence lifetimes of these states can be relatively long.[1,3] Naphthalene-2-carbaldehyde, methyl 2-naphthyl ketone, and 2-naphthyl phenyl ketone possess lowest triplet states of the π,π^* type,[4] and we now report that the e.s.r. spectra of the triplet states of these compounds can be observed.

The spectra of u.v.-irradiated samples of naphthalene-2-carbaldehyde, methyl 2-naphthyl ketone, and 2-naphthyl phenyl ketone in EPA (ether–isopentane–ethanol) glass at 77°K exhibit typical triplet-state signals with a relatively intense "$\Delta m = 2$" transition and weak "$\Delta m = 1$" transitions. In contrast to the spectra of carbonyl derivatives of benzenoid compounds, where only the "$\Delta m = 2$" transition can be observed,[5] the spectra of the compounds studied herein show four of the six "$\Delta m = 1$" transitions. Analysis

of the spectra gave the parameters for the spin–spin interaction listed in the Table.

E.s.r. parameters for the triplet states of some derivatives of naphthalene

Compound	D	E	$(D^2 + 3E^2)^{\frac{1}{2}}$	D^*
Naphthalene-2-carbaldehyde	0·094	0·029	0·106	0·102
Methyl 2-naphthyl ketone	0·096	0·027	0·107	0·105
2-Naphthyl phenyl ketone	0·095	0·026	0·105	0·105
[$^2H_8$]Naphthalene†	0·100	0·015	0·103	0·101

† E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 1964, **41**, 1763.

The values of the composite term D^* calculated from the position of the "$\Delta m = 2$" transition[6] are in agreement with the values for the equivalent term $(D^2 + 3E^2)^{\frac{1}{2}}$ calculated from the positions of the "$\Delta m = 1$" transitions. It can be seen from the Table that the values of D for the carbonyl derivatives of naphthalene are less than that for [$^2H_8$]naphthalene whilst the corresponding values of E are greater. The smaller values of D for the carbonyl derivatives of naphthalene as compared to the value for [$^2H_8$]naphthalene reflect the extended conjugation and the lower degree of interaction between the unpaired electron spins in the former compounds. The higher values of E are a measure of the lower symmetry of the carbonyl compounds.

Since aromatic carbonyl compounds possessing lowest triplet states of the π,π^* type can exhibit triplet-state signals whereas those with lowest triplet states of the n, π^* type do not, the e.s.r. technique may be used in certain cases to characterise lowest triplet states. However, the absence of a triplet-state signal does not necessarily mean that the lowest triplet state of the carbonyl compound is of the n, π^* type since the phosphorescence lifetimes of π,π^* states can be too short to allow detection.

The e.s.r. parameters of aromatic carbonyl compounds may provide evidence as to the relationship between the electronic distribution of triplet states and the chemical reactivity of these states.

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Mass Spectra of Isomers. Part III.[1] Cyclo-octadiene and Derivatives of Cyclobutane and Cyclohexene of Molecular Formula C_8H_{12}

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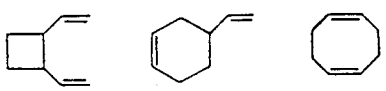
The mass spectra of *trans*-1,2-divinylcyclobutane, 4-vinylcyclohexene and 1,5-cyclo-octadiene have been examined. The similarity between the spectra of these compounds is probably a consequence of a major fragmentation pathway in each compound proceeding through a common intermediate, while the differences in the relative abundances of some of the ions is postulated as being a result of alternative routes for fragmentation of the isomers. The values of $100/\Sigma I$ for the major ions at electron beam energies of 70 and 20 ev are reported and interpreted in terms of the proposed fragmentation routes.

ALTHOUGH the mass spectra of geometric [2] and of positional isomers [2-4] are essentially similar, their spectra often exhibit differences in the relative abundances of some of the fragment ions. In continuation of a study of the relationship between the structures of isomers and the relative abundances of the ions formed upon electron impact, the mass spectra of *trans*-1,2-divinylcyclobutane (I), 4-vinylcyclohexene (II), and 1,5-cyclo-octadiene (III) have been examined. The mass



(I) (II) (III)

spectral data for compounds (I)—(III) are presented in Table 1. It can be seen that, while essentially the same fragment ions are formed from each compound, there are considerable differences in the relative intensities of some of the ions. Compounds (I)—(III) were prepared by the photodimerisation of 1,3-butadiene (M, 54) and since the base peaks in the spectra are at m/e 54 it is apparent that the compounds readily fragment to the monomer ion upon electron impact; charge retention in the monomer fragment of 4-vinylcyclohexene has been investigated by Smith and Thornton.[5]

The mass spectra of the compounds below m/e 54 are similar to that of butadiene and this region of the spectra is not discussed.

TABLE 1

Mass spectra (70 ev) (relative intensity: m/e 54 = 100)

m/e	(I)	(II)	(III)	m/e	(I)	(II)	(III)
26	3	2	2	65	4	7	9
27	18	17	19	66	6	36	16
28	6	3	6	67	12	26	80
29	2	3	3	68	1	2	5
38	2	2	3	77	7	15	13
39	39	37	46	78	5	13	6
40	2	3	4	79	28	60	38
41	10	18	21	80	16	32	42
50	4	4	5	81	2	3	3
51	7	9	9	91	3	9	7
52	5	5	5	93	9	18	12
53	13	11	13	94	1	1	—
54	100	100	100	107	1	1	1
55	5	5	5	108	0·3	9	5
63	2	2	3				

The major ions above m/e 54 appear at m/e 66, 67, 77, 78, 79, 80, and 93 and a scheme indicating the origin of these ions is shown in Scheme 1. This scheme is based upon the previously reported fragmentation routes [1,3] of derivatives of cyclobutane and cyclohexene which are similar in structure to compounds (I) and (II). The present scheme incorporates the fragmentation

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[2] P. Natalis, 'Mass Spectrometry, NATO Advanced Study,' ed. R. I. Reed, Academic Press, 1964, p. 379.
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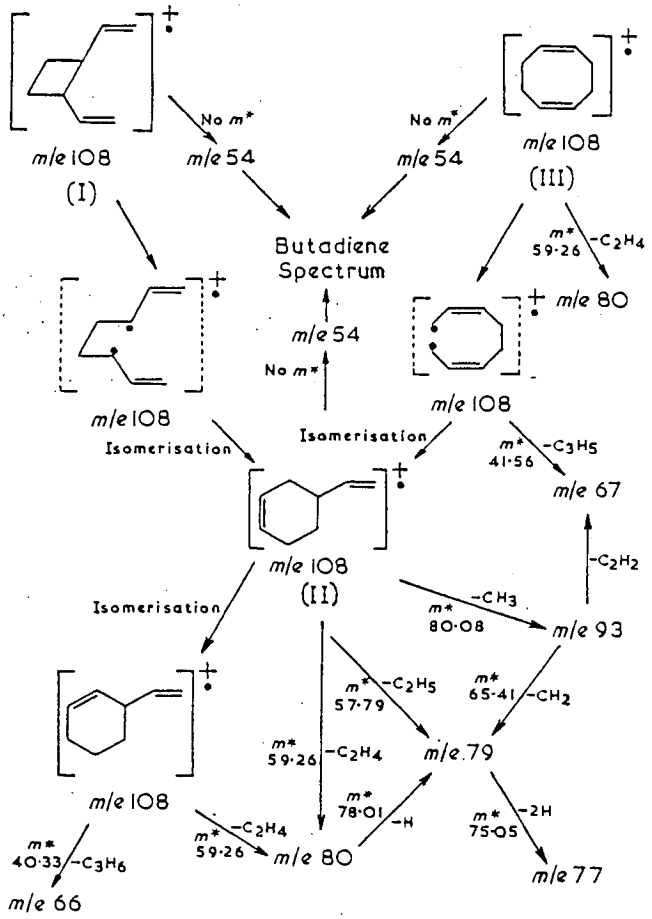


SCHEME 1 Major fragmentation routes of *trans*-1,2-divinylcyclobutane (I), 4-vinylcyclohexene (II), and 1,5-cyclo-octadiene (III)

pathways of the molecular ion of 1,5-cyclo-octadiene (III) and it is postulated that this ion, like the molecular ion of compound (I), can undergo isomerisation to the molecular ion of compound (II) and that the breakdown of this latter ion contributes to the peak intensities of the ions observed in the mass spectra of compounds (I) and (III).

This postulate is reasonable in view of the similarity between the spectra of compounds (I)—(III) and the difficulty of proposing an alternative fragmentation route leading to the ions of *m/e* 66 and 79 from the molecular ions of compounds (I) and (III). Formation of the ions of *m/e* 66 and 79 to a significant extent in the spectra of compounds (I) and (III) indicates that the molecular ion of compound (II) is formed when compounds (I) and (III) are subjected to electron impact.

The molecular ions of compounds (I) and (III) would not be expected to isomerise totally to the molecular ion of compound (II) and certain of the ions formed from compounds (I) and (III) will result from fragmentation of the molecular ion of the parent compound as well as from fragmentation of the isomerised form. The ions from compounds (I) and (III) which have a greater relative intensity than the corresponding ions from compound (II) must also be formed by a route other than that proceeding *via* the molecular ion of compound (II). On the other hand, ions from compounds (I) and (III) which have a lower relative intensity than the corresponding ions from compound (II) may, or may not, be produced by more than one route.

The only important ions in the spectra of compounds (I) and (III) which have a greater relative intensity than the corresponding ions from compound (II) are the ions of *m/e* 67 and 80, formed from compound (III). The ion of *m/e* 67, which corresponds to loss of $C_3H_5^{\bullet}$ from the molecular ion of compound (III), may be formed *via* the routes illustrated in Scheme 2.

Isomerisation (A) can proceed by addition of the free radical at C-1 to the olefinic system at C-6 with subsequent bond rearrangement to give the molecular ion of compound (II). Fragmentation of this ion by the route indicated will give the ion of *m/e* 67. Isomerisation (B) involves hydrogen-atom migration and bond rearrangement, and results in an open-chain molecular ion from which a $C_3H_5^{\bullet}$ fragment may be lost by bond fission.

The ion of *m/e* 80 in the spectrum of compound (III) is produced by the loss of a molecule of ethylene which can occur by a simple fragmentation process and so may be expected to compete with the isomerisation process which leads to the formation of the molecular ion of compound (II).

The molecular ion of compound (I) would also be expected to fragment directly to the ion of *m/e* 80. However, as indicated by the relative intensity of the ion of *m/e* 80 from compound (I) as compared with the relative intensities of this ion from compounds (II) and (III), this fragmentation route does not compete so effectively with the isomerisation route as does the corresponding fragmentation route in compound (III).

It is significant that the spectra of compounds (I)—(III) are markedly different from the spectra of trimethylcyclopentadienes [4] although both sets of compounds are isomers of molecular formula C_8H_{12}. The difference between the spectra is probably due to the intermediate in the fragmentation of compounds (I)—(III) being the molecular ion of compound (II), whereas the intermediate in the fragmentation of the trimethylcyclopentadienes is a cyclic benzenium species.[4]

The mass spectrum of 1,5-cyclo-octadiene (III) reported in this paper is identical with that reported by Harrison *et al.*[4] and is similar in many respects to the spectrum of 1,3-cyclo-octadiene reported by those authors. One main difference between the spectra of 1,5-cyclo-octadiene and 1,3-cyclo-octadiene is that the ion of *m/e* 54 is the most abundant ion in the spectrum of the former compound, whereas it is only present in relatively small amounts in the spectrum of the latter compound. This is to be expected since the ion of *m/e* 54 can be formed by direct dissociation of the molecular ion of 1,5-cyclo-octadiene whilst to obtain an ion of *m/e* 54 from 1,3-cyclo-octadiene bond migration must occur in the molecular ion prior to dissociation.

On the other hand the loss of a $C_2H_5^{\bullet}$ fragment from the molecular ion of 1,5-cyclo-octadiene involves bond migration and hence does not readily occur. The corresponding loss from the 1,3-cyclo-octadiene occurs readily without bond migration and, as a result, the relative intensity of the ion of *m/e* 79 in the spectrum of 1,3-cyclo-octadiene is much greater than the value for this ion in the spectrum of 1,5-cyclo-octadiene.

Values of $100I/\Sigma I$. The intensities of the ions shown in Scheme 1 are given in Table 2 as $100I/\Sigma I$ values for spectra recorded at electron-beam energies of 70 and 20 ev. The values of $100I/\Sigma I$ for the molecular ions are a measure of the relative stability of the ions [6] and the results shown in Table 2 indicate that the stabilities

TABLE 2

Values of $100I/\Sigma I$ at 70 ev and 20 ev for the major ions from compounds (I)—(III)

	(I)		(II)		(III)	
m/e	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev
108	0·09	0·21	2·05	2·75	1·07	1·90
93	2·67	4·85	4·00	6·06	2·49	3·62
80	4·72	6·74	6·92	11·11	8·52	13·00
79	8·54	10·96	12·17	16·99	7·23	8·36
77	2·22	1·16	3·24	1·88	2·63	1·39
67	3·70	5·69	5·59	6·85	16·21	26·92
66	1·77	3·09	7·84	13·06	3·24	5·15
54	30·06	42·14	21·77	25·48	20·24	24·14

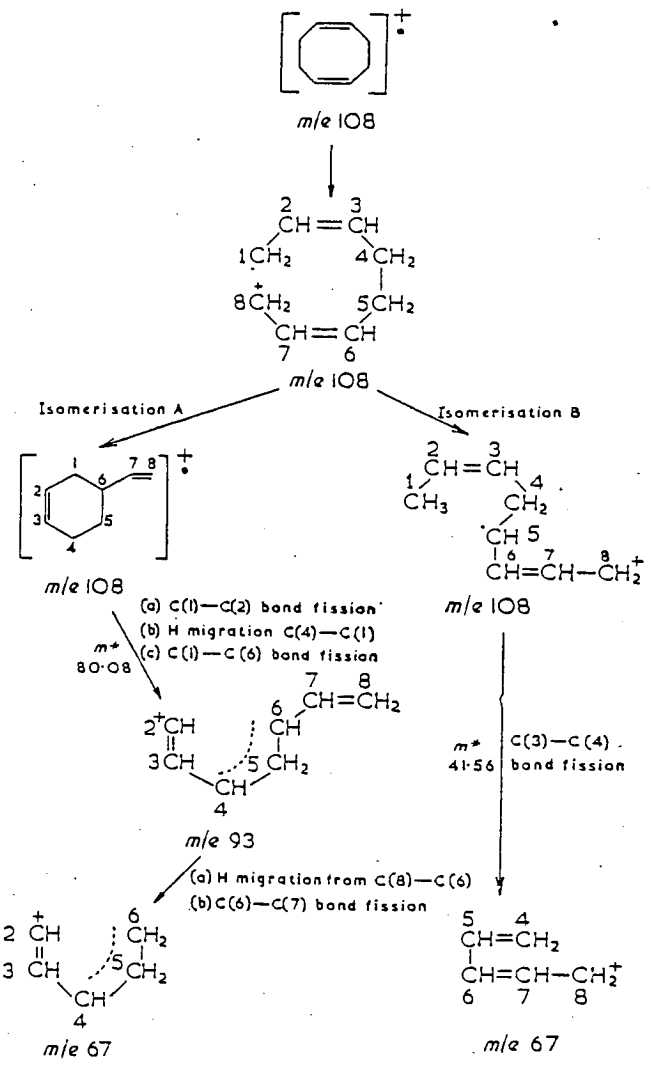
of the molecular ions of compounds (I)—(III) are in the order (II) > (III) > (I). The observation that the molecular ion of compound (II) has the greatest stability is in accord with the evidence that the molecular ions of compounds (I) and (III) isomerise to the molecular ion of compound (II). The relatively large values of $100I/\Sigma I$ for the ion of *m/e* 54 from compound (I) compared with the corresponding values for this ion from compounds (II) and (III) are presumably a consequence of the molecular ion of compound (I) being the least stable of the molecular ions.

The values of $100I/\Sigma I$ for the ions produced from the major fragmentation routes generally increase when the electron-beam energy is decreased. This is because all the ions listed, with the exception of *m/e* 77, are primary fragments which result directly from fission of the molecular ion. The ion of *m/e* 77, on the other hand, is not formed directly from the molecular ion and therefore its intensity decreases when the electron-beam energy is lowered.

On changing the electron-beam energy from 70 to 20 ev the increase in the value of $100I/\Sigma I$ for the ion of *m/e* 67 is greater in compound (III) than in compound (II). This is compatible with the suggestion that the ion of *m/e* 67 from compound (III) is formed by two routes (see Scheme 2).

EXPERIMENTAL

The mass spectral data given in Tables 1 and 2 were obtained with an A.E.I. MS2 instrument operating at an electron-beam energy of 70 ev and 20 ev. Samples were injected through a gallium inlet-sinter at 100°. Metastable peaks were observed in spectra recorded on an A.E.I. MS9 instrument at N.P.L. The corresponding metastable



SCHEME 2 Competing fragmentation processes which lead to the ion of *m/e* 67

transitions were confirmed by observation, with a device fitted to the instrument,[7] of the decompositions occurring in the field-free region between the source and the electrostatic analyser. Compounds (I)—(III) were prepared by the photodimerisation of 1,3-butadiene.[8] The compounds were purified by gas-phase chromatography and characterised by i.r. and n.m.r. spectroscopy and by measurement of refractive index.

The authors gratefully acknowledge the experimental assistance given by Miss J. Grice (Kingston).

[8/1790 *Received, December 5th*, 1968]

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A Charge-transfer Complex of a Substituted Tetrazaborol-2-ine

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A Charge-transfer Complex of a Substituted Tetrazaborol-2-ine

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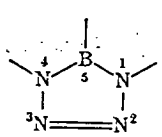
Summary The parameters of the charge-transfer interaction of 1,4,5-trimethyltetrazaborol-2-ine with 1,3,5-trinitrobenzene, studied by n.m.r., have indicated probable $n \rightarrow \pi$ rather than $\pi \rightarrow \pi$ interactions.

THERE has been considerable interest recently in heterocyclic boron–nitrogen compounds,[1] particularly in view of potential π-electron delocalisation in a number of these systems. The tetrazaboroline ring (1), which may be visualised as a five-membered, six π-electron system, is strongly suggested to be planar on the basis of spectroscopic and other evidence,[1] and M. O. calculations[2] have indicated considerable π-delocalisation in the ring.



(1)

As part of a general study of the chemistry of this system, we have endeavoured to obtain direct, experimental

evidence for π-delocalisation and therefore examined the possibility of forming charge-transfer complexes of the tetrazaboroline system with suitable π-acceptors.

We have studied the charge transfer interaction of 1,4,5-trimethyltetrazaborol-2-ine with 1,3,5-trinitrobenzene in carbon tetrachloride solution at 33·5° using the n.m.r. method developed by Hanna and Ashbaugh[3] and modified by Foster and Fyfe.[4]

A least-squares plot of the ratio of the chemical-shift difference of the acceptor protons in the complexing medium and the uncomplexed state to the concentration of donor, $\Delta/[D]$, against the same chemical-shift difference, Δ, led to values of the association constant K and shift difference of the acceptor protons in the pure complex and those in the free acceptor, Δ_0, of respectively $5{\cdot}4_4$ kg. mole^{-1} and $8{\cdot}0_3$ Hz.

It is interesting to compare these data with the literature values for benzene, hexamethylbenzene, and *NN*-dimethylaniline donors with the acceptor 1,3,5-trinitrobenzene in carbon tetrachloride under similar conditions.[4] The observed value of K is very much larger than that which would have been expected for a $\pi \rightarrow \pi$ complex since it is comparable with the very strong π-donor hexamethylbenzene (5·1) and an order of magnitude larger than that of benzene (0·50). Although it is difficult to make comparisons with different acceptors in different solvents, it would appear that the association constant is vastly larger than that which hexamethylborazine might be expected to have with trinitrobenzene on the basis of the observed value of 1·17 with tetracyanoethylene in chloroform.[5] We were unsuccessful in obtaining the direct comparison with hexamethylborazine experimentally since further reaction occurred between the borazine and the trinitrobenzene during the time of the experiment. The observed K value is probably best accounted for by an interaction of different nature to that in benzene and hexamethylbenzene, and thus we suggest $n \rightarrow \pi$ interaction from the lone pairs at the 2- and 3-nitrogens. This is consistent with estimates of ionisation potentials of a lone-pair electron and removal of an electron from the highest filled molecular orbital in Me_2N_4BH.[2,6]

The small value of Δ_0 in the tetrazaboroline complex also correlates with an interaction which is different from the $\pi \rightarrow \pi$ complexes. It is of interest to note that pentamethylenetetrazole interacts with trinitrobenzene in carbon tetrachloride to give values of K and Δ_0 of 2·1 kg. mole^{-1} and *ca.* 6 Hz.[7] The authors suggested that this was a $\pi \rightarrow \pi$ charge transfer complex, but again we feel that this is more likely to be a similar $n \rightarrow \pi$ interaction.

(*Received, August 18th*, 1969; *Com.* 1263.)

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Studies on Nitroaromatic Compounds. Part I. Nuclear Magnetic Resonance Investigation of Complexes of Benzene with Trinitrotoluenes

By E. Shilton and C. H. J. Wells,* Department of Chemistry, Kingston Polytechnic, Kingston upon Thames Surrey

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Studies on Nitroaromatic Compounds. Part I. Nuclear Magnetic Resonance Investigation of Complexes of Benzene with Trinitrotoluenes

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The formation of complexes of benzene with the six isomeric trinitrotoluenes has been studied by n.m.r. spectroscopy. Chemical-shift data have shown that the relative positioning of the components within the complexes depends upon the placement of substituents in the trinitrotoluenes. Where possible, association constants (K_c) for complex formation have been evaluated from chemical-shift measurements on nonequivalent protons, and it has been found that for a particular acceptor the values of K_c so obtained are the same within experimental error. The relative stabilities of the complexes are discussed in terms of steric effects and Lewis acidities of the trinitrotoluenes.

NITROAROMATIC compounds can act as electron acceptors in the formation of charge-transfer complexes with suitable electron donors.[1] In the case of polynitrobenzenes, the stability of complexes formed with a single donor is dependent upon the number of substituent nitro-groups and, for isomeric species, the position of the substituents in the ring system.[2,3] Studies on the electron-acceptor properties of isomeric nitrobenzenoid compounds have been confined to the dinitro- and trinitrobenzenes, for which only three isomers are available in each series. In order to gain further insight into the complexing properties of isomeric species we have studied the complexes formed between benzene and the six isomeric trinitrotoluenes.

EXPERIMENTAL

Chemical-shift measurements were made on a Perkin-Elmer R10 n.m.r. spectrometer operating at 60·004 MHz. Tetramethylsilane was used as internal reference. Each measurement was made in triplicate and the results were averaged. The results were analysed using equation (1),[4]

$$\Delta/[D]_0 = -\Delta K_c + \Delta_0 K_c \qquad (1)$$

where $[D]_0$ is the total donor concentration, K_c is the association constant for formation of a 1 : 1 complex between donor and acceptor, Δ is the difference between the chemical shift of the acceptor protons in the presence and absence of the donor, and Δ_0 is the difference between the chemical shift of the acceptor protons in the uncomplexed acceptor and the fully complexed acceptor.

The values of K_c and Δ_0 (see Table) were evaluated from a least-squares plot drawn by an Elliot 4100 computer.

1,2-Dichloroethane was used as solvent and was fractionally distilled prior to use. Samples of the trinitrotoluenes were kindly supplied by Drs. I. Dunstan and R. Simkins of the Explosives Research and Development Establishment, Ministry of Technology.

RESULTS AND DISCUSSION

The values of K_c and Δ_0 given in the Table are for measurements made on the aliphatic and aromatic proton resonances of the trinitrotoluenes. In the case of the 2,3,4-, 2,3,5-, 2,3,6-, and 2,4,5-derivatives there are two magnetically nonequivalent aromatic protons which give rise to either two single bands or a pair of doublet bands in the spectra. The addition of benzene to the systems causes the resonances to move upfield, and in these particular derivatives either both aromatic resonances or the upfield partner eventually became obscured by the benzene and associated sideband resonances. Since it was desirable to make measurements over as wide a range of chemical shift as possible, measurements were not made on signals which became obscured. The results given in the Table for the aromatic resonances of the 2,3,5- and 2,4,5-trinitrotoluenes are for the downfield resonance in each case.

Association constants (K_c) and chemical-shift values (Δ_0) for complexes of benzene with isomeric trinitrotoluenes [a]

Trinitrotoluene	K_c [b,c] Al [e]	K_c [b,c] Ar [f]	Δ_0 [d] Al	Δ_0 [d] Ar
3,4,5-	0·16	0·17	75	83
2,3,4-	0·12	*g*	68	*g*
2,4,5-	0·15	0·13	64	72
2,3,5-	0·15	0·16	62	57
2,3,6-	0·11	*g*	54	*g*
2,4,6-	0·14	0·13	51	66

[a] Solvent: 1,2-dichloroethane; temperature: 33·5°. [b] In kg solution mol^{-1}. [c] Estimated error in quoted values is ±0·01 in each case. [d] In Hz. [e] K_c values derived from measurement of chemical shift of aliphatic protons. [f] K_c values derived from measurement of chemical shift of aromatic protons. In cases where two aromatic resonances were observed, measurements were taken on the position of the downfield resonance. [g] Aromatic proton resonances obscured by benzene and associated sideband resonances.

The values of K_c derived from measurements on nonequivalent protons in a particular acceptor are found to be the same within experimental error. This contrasts with previous findings for the benzene–2,4,6-trinitrotoluene complex (in carbon tetrachloride) where the values of K_c derived from the aliphatic and aromatic proton resonances were 0·21 and 0·42 kg solution mol^{-1} respectively.[5] The difference between these values was suggested [5] to have arisen because the stoicheiometry of the complex species was not restricted to 1 : 1. The

[1] See references cited in (*a*) L. J. Andrews and R. M. Keefer, 'Molecular Complexes in Organic Chemistry,' Holden-Day Inc., San Francisco, 1964; (*b*) R. Foster, 'Organic Charge-Transfer Complexes,' Academic Press, London, 1969.

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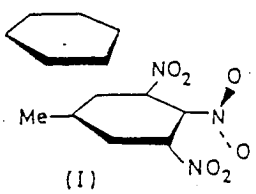
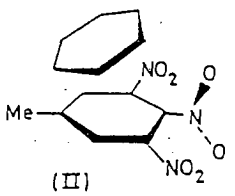
[5] M. I. Foreman, R. Foster, and D. R. Twiselton, *Chem. Comm.*, 1969, 1318.

observation that in 1,2-dichloroethane the values of K_c, obtained from measurements made on nonequivalent protons, are the same suggests that the stoicheiometry of the complexes is essentially 1 : 1 in this solvent. As is the case for other charge-transfer complexes,[6] the values of K_c for the benzene–2,4,6-trinitrotoluene system are lower in 1,2-dichloroethane than the corresponding values in carbon tetrachloride.

Evidence for the time-averaged relative orientations of the donor and acceptor components in a 1 : 1 complex can be gained from the values of Δ_0 for the different proton types in the acceptor moiety.[7] If, for example, there are two proton types then the protons with the larger value of Δ_0 will be closer to the centre of the complex. It can be seen from the Table that the values of Δ_0 for the aliphatic and aromatic protons of each acceptor differ and, also, that the values for the aliphatic protons can be broadly classified into three groups: those greater than 70 Hz, those between 60—70 Hz, and those less than 60 Hz. The values for the aliphatic and aromatic protons of 3,4,5-trinitrotoluene are of particular significance since it is only in this acceptor that the three nitro-groups are located at one end of the molecule leaving the aliphatic and aromatic protons 'exposed'. In the complex the benzene molecule will tend to be sited over the 1,2, and 6 positions of the acceptor rather than over the sterically crowded 3,4, and 5 positions and, in such a situation, both the aliphatic and aromatic protons will be close to the centre of the complex. The relative values of Δ_0 for the aliphatic and aromatic protons suggest that the aromatic protons lie closer to the centre of the complex than the aliphatic protons. Possible orientations of the components within the complex are as shown in structures (I) and (II).



(I)



(II)

In the benzene—2,4,6-trinitrotoluene complex it is the 1,2, and 6 positions of the acceptor which are sterically crowded, and here the benzene molecule would be expected to lie preferentially over the 3,4, and 5 positions. This is borne out by the fact that the value of Δ_0 for the aromatic protons is relatively high while for the aliphatic protons is the lowest recorded. Possible structures for this complex would be analagous to structures (I) and (II) with the methyl group and central nitro-group interchanged. The Δ_0 value for the aliphatic protons in the benzene–2,3,6-trinitrotoluene complex also falls within the group having Δ_0 less than 60 Hz. Here again the 1,2, and 6 positions in the acceptor are substituted and, presumably as a consequence, the aliphatic protons are relatively far removed from the centre of the complex.

The Δ_0 values for the aliphatic protons in those complexes in which one of the positions *ortho* to the methyl group is substituted fall in the range 60—70 Hz and lie between the corresponding values for the complexes in which both *ortho* positions are substituted and the value for the complex in which the *ortho* positions are unsubstituted. Thus the proximity of the methyl group to the centre of the complex appears to depend upon the extent of substitution at the 2 and 6 positions in the acceptor. This in turn implies that the benzene molecule occupies different positions with respect to the methyl group in the different complexes.

The magnitude of the association constants (K_c) provide a measure of the stability of the complexes. The results shown in the Table for the aliphatic protons indicate that the complexes of benzene with the 2,3,4- and 2,3,6-trinitrotoluenes are the least stable. This can be rationalised in terms of steric crowding in the acceptor species.[3] The four substituents in the 2,3,4- and 2,3,6-trinitrotoluenes are in adjacent positions in the ring and the steric hindrance to the approach of the donor molecule will be greatest for these particular molecules. Also, steric interaction will cause the nitro-groups to be forced out of planarity with the ring, and the consequent decrease in the mesomeric effect of the nitro-groupings will be greatest for the 2,3,4- and 2,3,6-derivatives. Thus the Lewis acidity of these molecules would be expected to be lower than for the other, less sterically crowded, isomers.

There is no apparent clear-cut distinction between the stabilities of the complexes formed with the 2,3,5-, 2,4,5-, 2,4,6-, and 3,4,5-trinitrotoluenes. However the slightly higher average value of K_c for the complex with 3,4,5-trinitrotoluene suggests that this complex is the most stable. If the Lewis acidities of this group of trinitrotoluenes are similar, this would indicate that 3,4,5-trinitrotoluene presents the least steric impedance to the approach of the benzene molecule.

[0/676 *Received, April, 27th* 1970]

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Tetrahedron Letters No.45, pp.3919-3921, 1970. Pergamon Press. Printed in Great Britain.

CHARGE-TRANSFER COMPLEXING ABILITY OF 2-CHLORO-4,6-DICYANOPYRIMIDINE

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The nature of substituents in a molecule determines whether the molecule acts as an electron donor or electron acceptor in charge-transfer complexation. The π-electron system of aromatic compounds is often an electron donor site (1), but if electron withdrawing substituents are present this property may be reversed and the electron deficient π-system may act as an electron acceptor site (2). As part of a general study of the acceptor properties of electron deficient systems we are synthesising pyrimidines and purines carrying electron withdrawing substituents. A possible site for interaction with carcinogens is at a nucleic acid and although there are some observations of chemical interaction between aromatic hydrocarbons and purines, pyrimidines, and nucleic acids which refer to the solubilisation of the hydrocarbon (3), there are only a few reports of charge-transfer complexation in the purine-hydrocarbon and pyrimidine-hydrocarbon systems. Machmer and Duchesne (4) have reported evidence for charge-transfer complexation between adenine, guanine, cytosine, and thymine and the strong acceptor chloranil in dimethylsulphoxide solution, and Duchesne and co-workers (5) have reported charge-transfer complexation between some nucleosides and chloranil. Evidence for some type of complexing between thiamine and various indoles has been obtained from n.m.r. spectroscopy (6), but no charge-transfer bands have been reported for the purine-hydrocarbon and pyrimidine-hydrocarbon systems in which the heterocyclic species is the acceptor. We have synthesised 2-chloro-4,6-dicyanopyrimidine and wish to report on the electron acceptor ability of this compound.

The ability of 2-chloro-4,6-dicyanopyrimidine to form charge-transfer complexes is indicated by the appearance of a new absorption band in the visible region of the spectrum when electron donors such as anthracene, chrysene, and pyrene are added to a solution of the compound in chloroform. A straight line plot is obtained (Fig 1) when the energy corresponding to the peak maximum of this new band, for a series of donors, is plotted against the energy of the charge-transfer transition in the corresponding complexes with 1,3,5-trinitrobenzene.

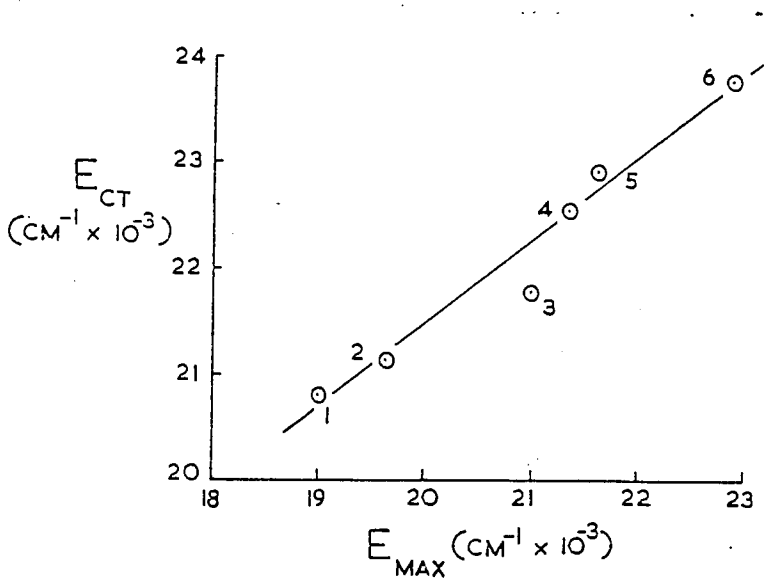

Fig. 1. Plot of energy (E_{max}, cm^{-1}) of peak maximum for a series of complexes of 2-chloro-4,6-dicyanopyrimidine against charge-transfer transition energy (E_{CT}, cm^{-1}) for the corresponding complexes of 1,3,5-trinitrobenzene.
The donors are: (1) perylene; (2) 3,4-benzopyrene; (3) anthracene: (4) pyrene; (5) 1,2-benzanthracene; (6) chrysene.

This demonstrates that the new band arises from a charge-transfer transition and, since the slope of the line is close to unity, it is evident that the complexes formed with 2-chloro-4,6-dicyanopyrimidine are of the same type as those formed with 1,3,5-trinitrobenzene, namely π,π complexes.

Association constants for complex formation are readily evaluated by the n.m.r. method developed by Hanna and Ashbaugh (7) and modified by Foster and Fyfe (8). The value of the association constant for the benzene/2-chloro-4,6-dicyanopyrimidine system in 1,2-dichloroethane at 33.5° is 0.65 kg mol^{-1}. This value may be compared with the value of 0.26 kg mol^{-1} for the association constant of the mesitylene/1,3,5-trinitrobenzene system in 1,2-dichloroethane at 33.5° (9). Since mesitylene is a more powerful electron donor than benzene (10) it is apparent that 2-chloro-4,6-dicyanopyrimidine is a better electron acceptor than 1,3,5-trinitrobenzene.

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Electron acceptor ability of some thioanhydrides

by G. L. O. Davies, G. A. Roff and C. H. J. Wells

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Anhydride and thioanhydride groups are electron withdrawing and when bonded to atoms in a π-electron system cause a charge deficiency in the π-system. This is exemplified by the ability of anhydrides, such as maleic and tetrachlorophthalic anhydride, to act as electron acceptors in the formation of charge-transfer complexes with electron donor molecules.[1] The electron affinity of such anhydrides is related to the charge deficiency in the π-system and can be evaluated from the energy of charge-transfer from the highest occupied molecular orbital of the donor to the lowest vacant molecular orbital of the acceptor.[2] Although the electron affinities of a number of anhydrides have been measured in this way,[2,3] there are no reported values, as far as is known, for the electron affinities of thioanhydrides. In view of this, the authors have measured the energy of the charge-transfer transition in a number of complexes involving dichloromaleic thioanhydride (DCMTA), phthalic thioanhydride (PTA) and pyromellitic dithioanhydride (PMDTA) (Table I) and have calculated the electron affinities of these thioanhydrides using the equations derived by Briegleb.[2] The calculated electron affinities are given in Table II.

Table I

Energy of charge-transfer (ev) *in complexes of thioanhydrides with aromatic hydrocarbons* (*Solvent – carbon tetrachloride*)

Donor / *Acceptor*	*Hexamethylbenzene*	*Pyrene*	*Acenaphthene*
Dichloromaleic thioanhydride	3·01	2·92	2·96
Phthalic thioanhydride	3·28	3·10	
Pyromellitic dithioanhydride	2·76	2·49	2·61
p-Chloroanil[a]	2·40	2·04	2·25

[a] The energy of the charge-transfer transition in complexes of *p*-chloranil are included in the Table since these values are used in the calculation of electron affinities by method II of Table II

The mean values for the electron affinities of dichloromaleic thioanhydride, phthalic thioanhydride and pyromellitic dithioanhydride obtained from the results given in Table II are 0·61, 0·38 and 0·96 *ev* respectively. These values may be compared with the literature values for the electron affinities of dichloromaleic anhydride (0·55 *ev*),[3] phthalic anhydride (0·10 *ev*)[2] and pyromellitic dianhydride (0·86 *ev*).[2] Thus it is apparent that thioanhydrides are better electron acceptors than their anhydride analogues. This is in agreement with the previous qualitative findings that phthalic thioanhydride is a better electron acceptor than phthalic anhydride.[4]

Table II

Electron affinities (ev) *of dichloromaleic thioanhydride* (*DCMTA*), *phthalic thioanhydride* (*PTA*) *and pyromellitic dithioanhydride* (*PMDTA*)

	Method of calculation[a] *(I)*	*(II)*	*(III)*	*(IV)*
DCMTA complexes				
Hexamethylbenzene		0·76	0·64	0·69
Pyrene	0·50	0·49	0·53	0·59
Acenaphthene		0·66		
PTA complexes				
Hexamethylbenzene		0·49	0·37	0·42
Pyrene	0·32	0·31	0·34	0·41
PMDTA complexes				
Hexamethylbenzene		1·01	0·90	0·94
Pyrene	0·93	0·92	0·97	0·98
Acenaphthene		1·01		

[a] Reference 2: I – equation (23′); II – equation (25); III – equations (28′) and (30); IV – equation (33)

The more powerful electron acceptor properties of thioanhydrides may be rationalised in terms of the larger outer valence shell of the sulphur atom compared to that of the oxygen atom, and the consequent greater degree of electron delocalisation in the thioanhydride system. Just as for thiophen and furan, the sulphur-containing molecule has the greater 'aromaticity' and a relatively lower electron density in the π-electron system. As a result of this lower electron density, thioanhydrides would be expected to be better acceptors than the corresponding anhydrides.

Dr J. Idris Jones of the National Physical Laboratory is thanked for a gift of samples of the thioanhydrides.

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Mass Spectra of Isomers. Part IV.[1] Dinitronaphthalenes

By E. F. H. Brittain* and C. H. J. Wells, Kingston Polytechnic, Kingston upon Thames, Surrey
H. M. Paisley, Division of Chemical Standards, National Physical Laboratory, Teddington, Middlesex
D. J. Stickley, Perkin-Elmer Ltd., Beaconsfield, Buckinghamshire

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1970

Mass Spectra of Isomers. Part IV.[1] Dinitronaphthalenes

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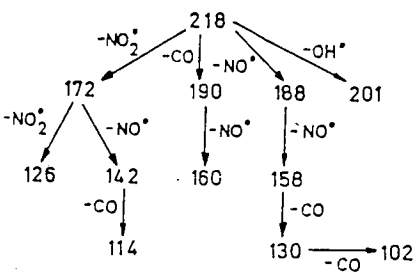
The mass spectra of the ten isomeric dinitronaphthalenes have been examined. The differences between the spectra have been accounted for in terms of the relative electron densities at the 8-position, steric interactions, and alternative fragmentation pathways.

THE mass spectra of mononitroaromatic compounds have been fairly extensively investigated and the fragmentations associated with the nitro-group have been well characterised.[2] The effect on the spectra of further substitution with nitro-groupings has, however, received relatively little attention. The introduction of a second strongly electronegative entity can have a marked effect on the fragmentation pattern of the molecule, the effect being dependent upon the relative positions of the substituents.[3,4] Beynon, Job, and Williams have discussed the elimination of CO from the molecular ions of the 1,3-, 1,4-, 1,5-, and 1,8-dinitronaphthalenes.[5] The mass spectra of the ten isomeric dinitronaphthalenes are now presented and discussed in more general terms.

The mass spectra of the dinitronaphthalenes are shown in the Figure. The major peaks in the spectra from *m/e* 114 upwards are readily assigned on the basis of the expected losses [6-8] of $NO_2^{\bullet}$, CO, NO·, and OH· either singly or in combination (Scheme 1). As would



SCHEME 1 Principal fragmentation routes in the mass-spectra of dinitronaphthalenes

be expected for isomers, the overall patterns of the spectra are similar. However comparison of the spectra

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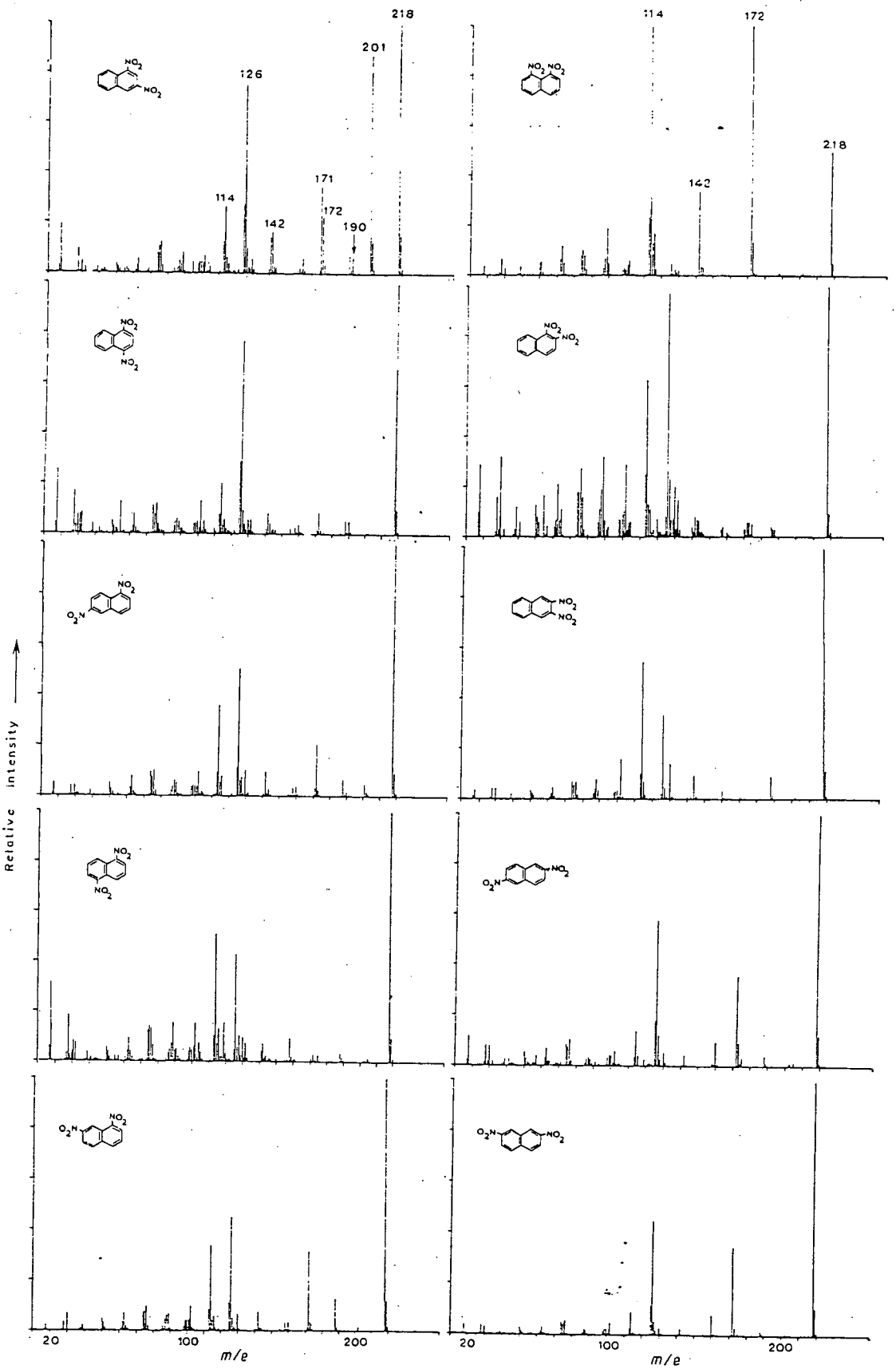
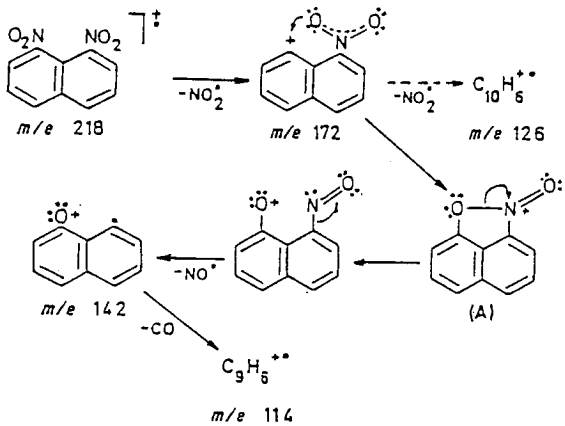


Mass spectra of dinitronaphthalenes

shows that there are significant differences in the relative intensities of the ions at certain *m/e* values.

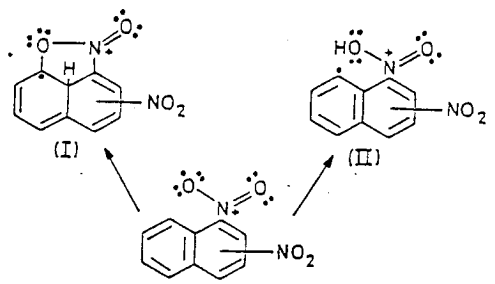
Comparison of the spectrum of 1,8-dinitronaphthalene with the other spectra in the Figure reveals several notable features in the former spectrum, namely a relatively small molecular ion peak, relatively large peaks at *m/e* 172, 142, and 114 and only a small peak at *m/e* 126. The relative instability of the molecular ion of 1,8-dinitronaphthalene must be the result of some form of interaction between the nitro-groups in the *peri*-positions where considerable overlap of the electron clouds associated with the oxygen atoms in the different nitro-groups would be expected. The detailed nature of the interaction is still, however, open to surmise. The peak at *m/e* 172 ($M - NO_2\cdot$) is considerably larger in the spectrum of the 1,8-derivative than in the others, suggesting that in this isomer the ion is either more readily produced from the molecular ion, or fragments by a different mechanism from that which operates for the other compounds. The observation that the peak arising from the ion of *m/e* 126 is very small for 1,8-dinitronaphthalene is significant in this respect since the presence of a metastable peak at *m/e* 92·30 in the spectra of the other derivatives shows that this ion is derived directly from the ion of *m/e* 172 by loss of the second nitro-group. Thus it appears that this loss is hindered in the 1,8-derivative, presumably because of the positive charge residing at the 8-position, and that the ion of *m/e* 172 derived from 1,8-dinitronaphthalene must mainly fragment by some alternative pathway. The presence of a positive charge at the 8-position, taken in conjunction with the lone-pair electron density on the oxygen of the remaining nitro-group, would favour the formation of the intermediate structure [A] shown in Scheme 2. Subsequent isomerisation of this intermediate, followed by loss of NO· and then CO as shown in Scheme 2 would explain the formation of the ions of *m/e* 142 and 114. The relatively large peaks due to these ions in the spectrum of 1,8-dinitronaphthalene can therefore be explained on the basis of this different fragmentation route for the ion of *m/e* 172 derived from the 1,8-derivative, although it should be noted that ions of *m/e* 142 and 114 are produced to some extent from all of the isomers, possibly *via* rearrangement of the *m/e* 172 species to the nitrite form.[7]



SCHEME 2 Fragmentation pathways in 1,8-dinitronaphthalene

Mechanisms for the loss of CO from the molecular ions of the 1,3-, 1,4-, and 1,5-dinitronaphthalenes have been given by Beynon, Job, and Williams.[5] They have explained the varying extents of this loss of CO in terms of the electron density at the 8-position; the higher the electron density in this position the greater the extent of the loss. The electron density at the 8-position in the 1-substituted derivatives (excluding 1,2-dinitronaphthalene) would be expected to be in the order 1,3- > 1,4- ≫ 1,6- > 1,5- > 1,7-, and hence the loss of CO, as measured by the intensity of the peak due to the ion of *m/e* 190, should also be in this order. Detailed examination of the spectra in the Figure reveals that the relative intensities of the peak at *m/e* 190 follow the expected order (changing from 5·9% for 1,3-dinitronaphthalene to 0·15% for 1,7-dinitronaphthalene, with a marked decrease between the 1,4- and 1,6-dinitronaphthalenes) although this order may be fortuitous since subsequent decomposition of the ion of *m/e* 190 may not be the same for the different isomers.

It has been suggested [5] that the loss of CO from the molecular ions of the dinitronaphthalenes could proceed by two mechanisms, the initial steps of which are shown in Scheme 3. It is to be expected that one of these



SCHEME 3

fragmentation routes would predominate, and an indication as to which route offers the lower-energy pathway for the majority of the isomers is given in the spectrum of 1,3-dinitronaphthalene. The spectrum of this derivative differs from those of the other isomers in that there are intense peaks at *m/e* 201 and *m/e* 171, and since these peaks correspond to loss of OH· and HONO respectively from the molecular ion it is probable that this compound fragments to an appreciable extent *via* species (II). Since the loss of OH· and HONO does not occur to any significant extent in the other compounds it may be concluded that fragmentation of species (I) is preferred to fragmentation of species (II) in these isomers. The loss of CO from the molecular ion of 1,3-dinitronaphthalene will also occur *via* species (I), and the observation made by Beynon *et al.*[5] that the extent of this loss is lower than would be predicted from

calculations of the electron density at the 8-position can thus be explained in terms of the existence of two competing fragmentation routes of similar energy. The formation of species (II) appears to be more markedly dependent on the electron density at the 8-position than is the formation of species (I). It is only for the 1,3-derivative, which has the highest electron density at this site, that fragmentation *via* species (II) becomes important.

The 1,2-derivative is anomalous compared with the other 1-substituted derivatives in that the loss of CO does not occur even though the electron density at the 8-position must be relatively high. This can be explained if the mechanism for CO loss involves the transfer of an oxygen atom from a nitro-group at the 1-position to the carbon atom at the 8-position and if the orientation of the nitro-group at the 1-position relative to the carbon atom at the 8-position is altered by steric interaction with a nitro-group at the 2-position so that the mechanism cannot operate.

The absence of a peak at *m/e* 190 from the spectra of the 2,3-, 2,6- and 2,7-dinitronaphthalenes is also in accord with the suggested mechanism for the loss of CO from the molecular ions.

EXPERIMENTAL

Mass spectra were obtained on a Perkin-Elmer–Hitachi RMS4 instrument operating at 70 ev with a 10 second per mass decade scan rate. During each scan total ion current readings remain constant. Samples were admitted by use of a direct insertion probe with probe temperature 80 °C, and ionisation chamber temperature 100 °C.

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SOLVENT EFFECTS ON THE ASSOCIATION OF BENZENE WITH 2,4,6-TRINITROTOLUENE

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The association constant for the formation of a 1:1 molecular complex between electron donor and electron acceptor species can be measured by a number of methods[1]. Of these, the n.m.r. method developed by Hanna and Ashbaugh[2] and modified by Foster and Fife[3] has been extensively used in recent years. Under the appropriate concentration conditions the n.m.r. method has been shown to give results which are internally consistent[4] and, also, results which are in reasonable agreement with those derived by optical methods[5]. However a recent communication[6] on association constants obtained by n.m.r. for a number of donor - acceptor systems reported that the value obtained is dependent on the particular nucleus in the acceptor upon which measurements are made. Carbon tetrachloride was used as solvent in the study, and since the results for the benzene-2,4,6-trinitrotoluene system conflicted with our findings for this system in 1,2-dichloroethane[7] we have now investigated the effect of solvent on the association constant for the interaction of benzene with 2,4,6-trinitrotoluene.

Chemical shift measurements were made on the aliphatic and aromatic protons of 2,4,6-trinitrotoluene(A) in the presence of excess benzene(D), and the values of the association constants, K^{AD}, were derived from a plot based on the equation

$$\Delta/D_o = K^{AD}\Delta_o - K^{AD}\Delta$$

where D_o is the initial concentration of donor D, Δ is the difference between the chemical shift of one of the acceptor proton types in the presence and absence of donor, and Δ_o is the difference between the chemical shift of the acceptor protons in the pure complex and in the uncomplexed acceptor. The values of the association constants in the different solvent systems are summarised in the Table.

It can be seen from the Table that there is a marked difference between the values of the association constants derived from measurements on the aliphatic and aromatic protons in the non-polar solvents carbon tetrachloride, carbon bisulphide, cyclohexane and n-hexane. As would be expected the values are lower in the relatively more polar solvents chloroform,

Association constants (K^{AD}) for the benzene(D)-2,4,6-trinitrotoluene(A) system under the condition $D_o \gg A_o$ and at 33.5°.

Solvent	K^{AD} (kg. mol^{-1})[a] Aliphatic protons	Aromatic protons
Carbon tetrachloride[b]	0.35	0.42
Carbon bisulphide	0.28	0.32
Cyclohexane	0.27	0.35
n-Hexane	0.23	0.31
Chloroform	0.20	0.22
1,2-Dichloroethane	0.14	0.13
Dichloromethane	0.12	0.14

[a]The error in the quoted values is ± 0.01 in each case. [b]Previous literature values for the aliphatic and aromatic protons in this solvent are 0.21 and 0.42 kg. mol^{-1} respectively[6].

1,2-dichloroethane and dichloromethane. As the values drop so the difference between the association constant within a system becomes masked. Since the differences are more marked in the non-polar set of solvents it would suggest that solute-solvent interaction is not the underlying cause of the anomaly in the values. It has been suggested previously[6] that the differences might arise from the presence in the system of isomeric 1:1 complexes or additional complexes in which the stoicheiometry is not confined to 1:1. The present results taken in conjunction with the previous findings indicate that association constants for weak interactions between donor and acceptor species must be viewed with caution.

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Introduction to Molecular Spectroscopy

Theory and Experiment

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Kingston-upon-Thames, England

1970

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Preface

Molecular spectroscopy has been the subject of a great deal of interest and activity in the past two decades. The early practitioners were mainly physicists but the subject has occupied an increasing share of the literature of chemistry both in relation to detailed fundamental studies of small molecules and to the necessarily more empirical studies of larger molecules.

The object of the present book is to present a balanced treatment of the principal methods of molecular spectroscopy together with selected practical work. The book is intended primarily for undergraduate courses in chemistry and represents the authors' experience in teaching the principles and applications of molecular spectroscopy to L.R.I.C., G.R.I.C. and B.Sc. students at both Ordinary and Honours level. Some of the subject matter is, however, covered in more detail than would normally be presented to undergraduates. This additional material, taken in conjunction with more advanced texts, has been used by the authors in a number of specialist short courses and in an M.Sc. course in molecular spectroscopy.

The book is limited to consideration of electronic, vibrational, nuclear magnetic resonance and mass spectrometry because of the general applicability of these methods and their availability to students. The first chapter is concerned with material which is common to different branches of molecular spectroscopy and an attempt has been made to present a unified approach to the underlying principles of the subject. Subsequent chapters deal with the different chosen branches in turn, and each chapter is divided into three sections—principles, instrumentation and experiments. The experiments have been designed largely to illustrate topics discussed in the principles and instrumentation sections, and cross-referencing to the appropriate experiments is given throughout the text.

We would like to express gratitude to many students and colleagues who have shared in the development of much of the material of this book and to Mr V. G. Mansell, Mr N. Falla and Miss J. Grice for valuable technical assistance. We are grateful also to Mr B. Haynes for the encouragement he has provided for the development of molecular spectroscopy within various courses in Kingston Polytechnic. Our thanks are also due to the staff of Academic Press who have provided considerable assistance and shown much patience.

April, 1970

E. F. H. BRITTAIN
W. O. GEORGE
C. H. J. WELLS

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Studies on Nitroaromatic Compounds. Part II.[1] An Electron Spin Resonance Study of the Radical Anions of Some Nitronaphthalic Anhydrides

By C. H. J. Wells * and J. A. Wilson, School of Chemical Science and Technology, Kingston Polytechnic, Kingston-upon-Thames

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Studies on Nitroaromatic Compounds. Part II.[1] An Electron Spin Resonance Study of the Radical Anions of Some Nitronaphthalic Anhydrides

By C. H. J. Wells * and J. A. Wilson, School of Chemical Science and Technology, Kingston Polytechnic, Kingston-upon-Thames

The radical anions of 2,5-dinitronaphthalic anhydride, 4,5-dinitronaphthalic anhydride, 2,4,5-trinitronaphthalic anhydride, and 2,4,5,7-tetranitronaphthalic anhydride have been prepared by reduction with sodium and their e.s.r. spectra have been recorded. Analysis of the spectra has yielded proton and nitrogen hyperfine coupling constants which are assigned, where possible, on the basis of molecular orbital calculations performed by use of the Hückel–LCAO method and the approximate configuration interaction method of McLachlan. The calculated π-electron spin densities agree well in most cases with experimental values. The radical-anion spectra have been simulated satisfactorily except in the case of the radical anion of 2,4,5-trinitronaphthalic anhydride where linewidth alternation alters the intensities of the lines in the spectrum.

POLYNITROAROMATIC compounds can act as electron acceptors and their radical anions can generally be formed by either electrolytic reduction,[2-6] photolytic reduction,[7-9] or by chemical reduction with alkali metals,[10-13] sodium dithionite,[14] or hydroxylamine.[15] The e.s.r. spectra of the radical anions of polynitrobenzenoid compounds have been extensively studied and shown to be dependent upon the solvent system and the method of preparation of the radical anion.[13,15,16-19] In many instances good agreement is found between the observed spectra and the spectra calculated on the basis of the expected interaction between the unpaired electron and the magnetically active nuclei in the system. However, in other cases, such as in the spectra of the dinitrobenzene radical anions, anomalies have been found in the linewidths and intensities of the observed lines.[20-22] These anomalies have been explained in terms of modulation of the hyperfine couplings either by migration of the cation between sites within the ion pair [23] or strong solvation of the radical anion.[15,21]

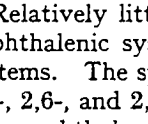
Relatively little work has been carried out on nitronaphthalenic systems in comparison to nitrobenzenoid systems. The spectra of the radical anions of 1,4-, 1,5-, 1,8-, 2,6-, and 2,7-dinitronaphthalenes and 1,4,5,8-tetranitronaphthalene have been analysed [13,15,24] and again line-broadening effects are observable in the spectra.[15] As part of a general study of the electron-acceptor properties of nitronaphthalenes, we have prepared the radical anions of 2,5-dinitronaphthalic anhydride, 4,5-dinitronaphthalic anhydride, 2,4,5-trinitronaphthalic anhydride, and 2,4,5,7-tetranitronaphthalic anhydride and have recorded their e.s.r. spectra in order to gain insight on the unpaired spin densities at sites within the naphthalene system and to ascertain whether any anomalous effects are apparent in the spectra. The results of this work are now reported.

RESULTS

The e.s.r. spectra of the radical anions are shown in Figures 1—4. The linewidths in all the spectra were 0·05 Oe except for the spectrum of 4,5-dinitronaphthalic anhydride where the linewidth is 0·10 Oe. The spectra can be explained in terms of isotropic nuclear–electron spin coupling for the appropriate proton and nitrogen atoms in the radical anions. The experimental coupling constants were checked by simulation of the spectra from the coupling-constant values and the peak to peak hyperfine linewidths by use of a computer programme based on a Lorentzian

TABLE 1

Molecular orbital parameters used in calculations

Substituent	Atom X	h_x	Bond X–Y	k_{X-Y}
C–NO_2	N	2·2	N–O	1·67
	O	1·4	C–N	*a*
	C*	−0·4	C–C*	1·25
	O′	2·0	C*–O′	1·6
	O″	1·2	C*=O″	1·0

[a] See Table 2 for values used for k_{C-N}.

[1] Part I, E. Shilton and C. H. J. Wells, *J. Chem. Soc.* (*B*), 1970, 1613.
[2] A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, 1961, **83**, 1852.
[3] L. H. Piette, P. Ludwig, and R. N. Adams, *J. Amer. Chem. Soc.*, 1961, **83**, 3909; 1962, **84**, 4212.
[4] M. T. Melchior and A. H. Maki, *J. Chem. Phys.*, 1961, **34**, 471.
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[6] P. H. H. Fischer and C. A. McDowell, *Mol. Phys.*, 1964, **8**, 357.
[7] C. Lagercrantz and M. Yhland, *Acta Chem. Scand.*, 1962, **16**, 1799.
[8] R. L. Ward, *J. Chem. Phys.*, 1963, **38**, 2588.
[9] W. T. Dixon and R. O. C. Norman, *Nature*, 1962, **196**, 891.
[10] T. L. Chiu, G. E. Pake, D. E. Paul, J. Townsend, and S. I. Weissman, *J. Phys. Chem.*, 1953, **57**, 504.
[11] R. L. Ward and M. P. Klein, *J. Chem. Phys.*, 1958, **28**, 518.
[12] R. L. Ward, *J. Amer. Chem. Soc.*, 1961, **83**, 1297.
[13] F. Gerson and R. N. Adams, *Helv. Chim. Acta*, 1965, **48**, 1539.
[14] P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, 1964, 1136.
[15] C. J. W. Gutch, W. A. Waters, and M. C. R. Symons, *J. Chem. Soc.* (*B*), 1970, 1261.
[16] M. J. Blandamer, T. E. Gough, J. M. Gross, and M. C. R. Symons, *J. Chem. Soc.*, 1964, 536.
[17] J. M. Gross and M. C. R. Symons, *Mol. Phys.*, 1965, **9**, 287.
[18] M. J. Blandamer, J. M. Gross, and M. C. R. Symons, *Nature*, 1965, **205**, 591.
[19] J. M. Gross and M. C. R. Symons, *Trans. Faraday Soc.*, 1967, **63**, 2117.
[20] J. H. Freed, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 1881.
[21] C. J. W. Gutch and W. A. Waters, *Chem. Comm.*, 1966, 39.
[22] R. L. Ward, *J. Chem. Phys.*, 1962, **36**, 1405.
[23] T. A. Claxton, W. M. Fox, and M. C. R. Symons, *Trans. Faraday Soc.*, 1967, **63**, 2570.
[24] P. H. H. Fischer and C. A. McDowell, *Canad. J. Chem.*, 1965, **43**, 3400.

line-shape function. The simulated spectra are also shown in Figures 1—4.

The values used in the molecular orbital calculations for the parameters h_x and k_{x-y} in the Coulomb integral $\alpha_x = \alpha + h_x\beta$ and the resonance integral $\beta_{xy} = k_{x-y}\beta$ respectively are given in Table 1. The values for the C–NO_2 group are those of Rieger and Fraenkel [25] with the resonance integral parameter k_{C-N} modified (see Table 2) to take into account steric interaction between the *peri* nitro-groups in the radical anions of 4,5-dinitronaphthalic anhydride, 2,4,5-trinitronaphthalic anhydride, and 2,4,5,7-tetranitronaphthalic anhydride and between the anhydride group and the *ortho* nitro-group or -groups in the radical anions of 2,5-dinitronaphthalic anhydride, 2,4,5-trinitronaphthalic anhydride, and 2,4,5,7-tetranitronaphthalic anhydride. The parameters for the anhydride group are those of Sioda and Koski [26] with the exception of k_{C-C^*} which was given a value of 1·25 instead of 1·0.

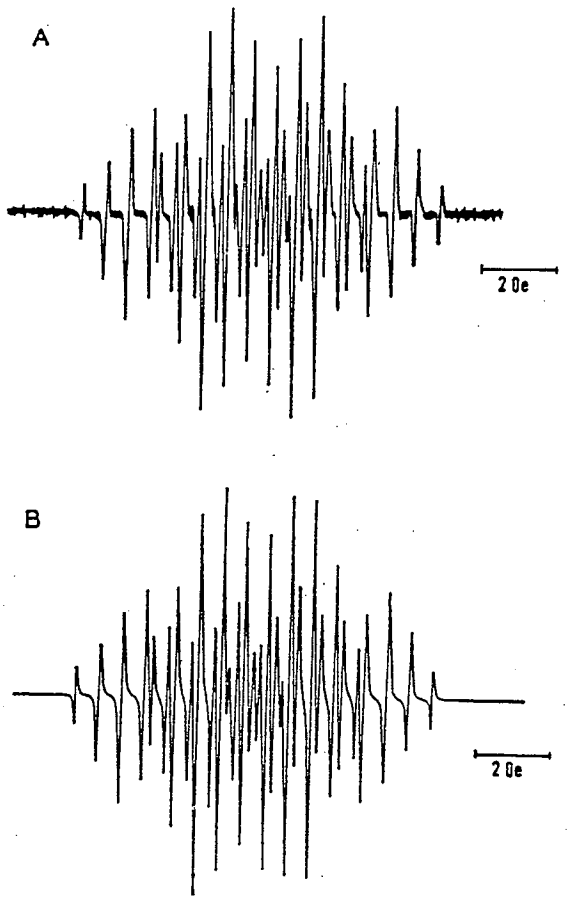


FIGURE 1 The e.s.r. spectrum of the radical anion of 2,5-dinitronaphthalic anhydride at −40 °C; A, experimentally observed; B, simulated

The results of Hückel LCAO calculations for the unpaired spin densities in the systems studied are given in Table 3. The unpaired spin densities, ρ, were also calculated according to McLachlan's method [27] whereby configuration interaction is introduced into the simple Hückel theory. This involves introducing a perturbation into the Hückel spin densities such that

$$\rho_i = C^2_{ij} - \lambda\Sigma\pi_{is}C^2_{sj}$$

where C_{ij} is the coefficient of the ith atom in the jth molecular orbital containing the unpaired electron, C_{sj} is

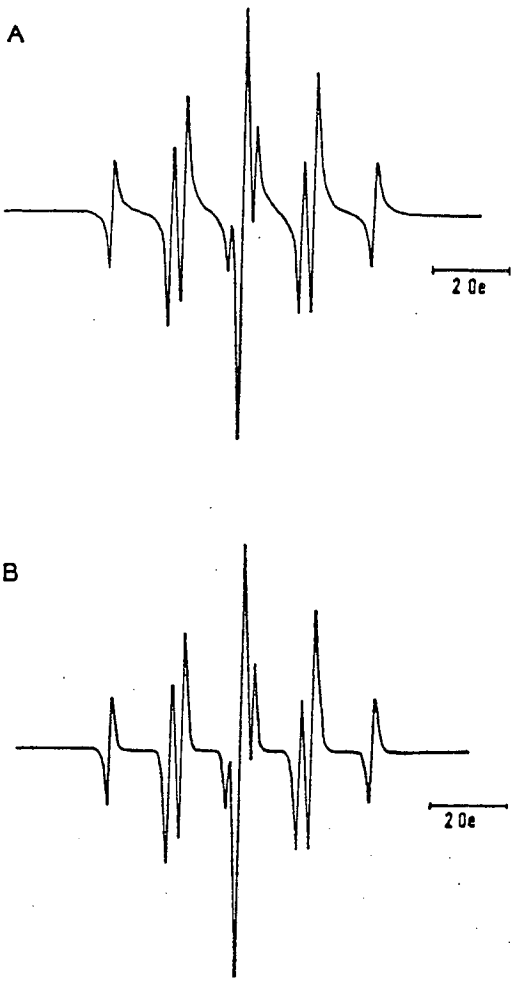


FIGURE 2 The e.s.r. spectrum of the radical anion of 4,5-dinitronaphthalic anhydride at −40 °C; A, experimentally observed; B, simulated

the coefficient of the sth atom in the same orbital, π_{is} is the atom–atom polarisability, and λ is an empirical constant

TABLE 2

Values of k_{C-N} used in calculations

Radical anion	Position of nitro-group	k_{C-N}
2,5-Dinitronaphthalic anhydride	2-	1·3
	5-	1·2
4,5-Dinitronaphthalic anhydride	4,5-	1·4
2,4,5-Trinitronaphthalic anhydride	2-	1·3
	4,5-	1·4
2,4,5,7-Tetranitronaphthalic anhydride	2,7-	1·3
	4,5-	1·4

[25] P. H. Reiger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609.

[26] R. E. Sioda and W. S. Koski, *J. Amer. Chem. Soc.*, 1967, **89**, 475.

[27] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

which normally takes the value 1·25. The unpaired spin densities calculated by the McLachlan procedure are given in Table 3. The experimental spin densities (Table 3) were derived from the McConnell equation [25] using a value of −23·7 Oe for the σ–π interaction parameter Q^{H}_{CH}.

The calculated nitrogen coupling constants, a_N, given in

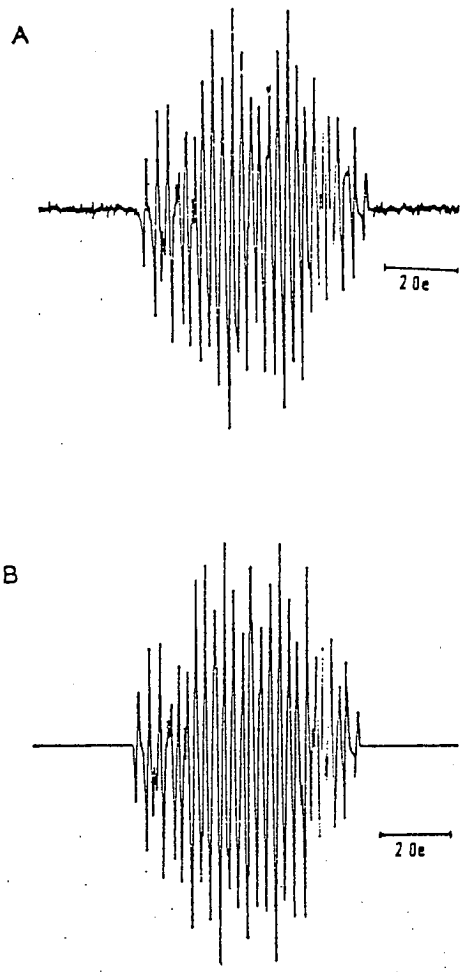


FIGURE 3 The e.s.r. spectrum of the radical anion of 2,4,5-trinitronaphthalic anhydride at −40 °C; A, experimentally observed; B, simulated

column 7 of Table 3, were obtained from Hückel spin densities by use of expression (1),[24] while the values given

$$a_N = \pm 179\rho_N^{\pi} \mp 149{\cdot}2\rho_O^{\pi} \pm 8{\cdot}06\rho_O^{\pi} \qquad (1)$$

in column 8 were obtained from McLachlan spin densities by use of expression (2),[25] where ρ_N, ρ_C, and ρ_O are the spin

$$a_N = \pm 99\rho_N^{\pi} \mp 71{\cdot}6\rho_O^{\pi} \qquad (2)$$

densities at the nitrogen nucleus and at the neighbouring carbon and oxygen nuclei respectively.

DISCUSSION

Except for the results for 2,4,5-trinitronaphthalic anhydride, the values for the calculated and experimental densities are in reasonable agreement (Table 3). This is illustrated in Figure 5 where the calculated spin densities obtained by the McLachlan method are plotted

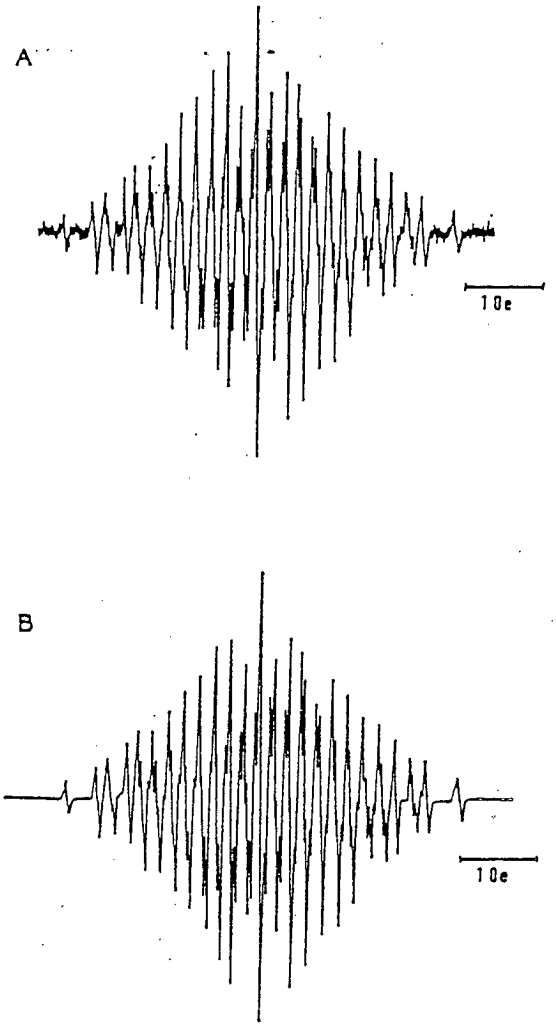


FIGURE 4 The e.s.r. spectrum of the radical anion of 2,4,5,7-tetranitronaphthalic anhydride at −40 °C; A, experimentally observed; B, simulated

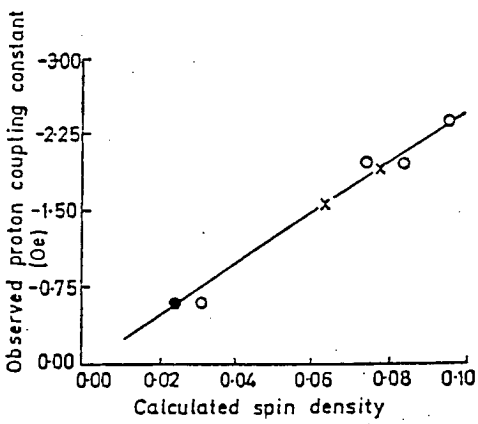


FIGURE 5 Proton correlation plot: ○ 2,5-dinitronaphthalic anhydride, × 4,5-dinitronaphthalic anhydride, and ● 2,4,5,7-tetranitronaphthalic anhydride

[25] H. M. McConnell, *J. Chem. Phys.*, 1956, **24**, 632.

against the experimentally observed proton coupling constants, the signs of which have been chosen to agree with the calculated signs of ρ and the negative sign of Q^{H}_{CH}. The straight line in the Figure represents absolute correlation and corresponds to $Q^{H}_{CH} = -23{\cdot}7$ Oe.

The spectrum of the radical anion of 2,5-dinitronaphthalic anhydride can be analysed in terms of nuclear–electron spin interaction involving two individual protons, two equivalent protons, and two equivalent nitrogen nuclei. The assignment of the two equivalent protons given in Table 3 must be regarded as tentative since the differences between the various calculated spin densities is not great enough to exclude any ambiguity. The assignment of the proton site of lowest spin density is fairly certain however. It is interesting that the nitrogen couplings in this radical anion are coincidently equivalent. This may reflect the *ortho,para* influence of the anhydride group tending to equalise the electron densities at these nuclei.

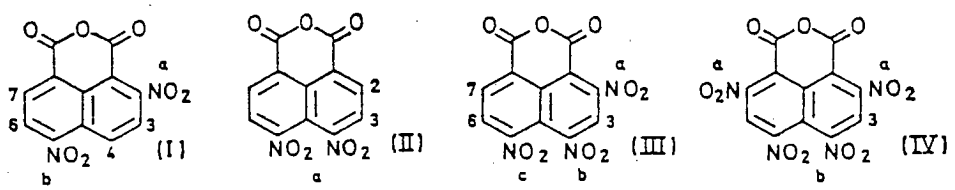
The agreement between the McLachlan and experimental spin densities for the 4,5-dinitronaphthalic anhydride radical anion is remarkably good and allows the proton coupling constants to be assigned with some degree of certainty. The noteworthy feature of the spectrum of this radical anion is the absence of nitrogen hyperfine interaction, even although the calculations using McLachlan spin densities predict a value of 0·4 Oe for the nitrogen coupling constant. The lack of nitrogen coupling with the *peri* nitrogen nuclei in 4,5-dinitronaphthalic anhydride is to be contrasted with the coupling constants of 7·5 and 0·25 Oe found for *peri* nitrogen interaction in the sodium–1,8-dinitronaphthalene and sodium–1,4,5,8-tetranitronaphthalene ion-pairs

TABLE 3

Calculated and experimental parameters for nitronaphthalic anhydride radical anions

Radical anion	Position	Spin densities			Proton coupling constants (Oe)	Nitrogen coupling constants (Oe)		
		Hückel	McLachlan	Expt.		Hückel [a]	McLachlan [b]	Expt.
(I)	O(a)	0·0547	0·0580	—	—	—	—	—
	N(a)	0·0388	0·0353	—	—	0·64	0·66	0·59
	O(b)	0·0650	0·0673	—	—	—	—	—
	N(b)	0·0462	0·0418	—	—	0·74	0·68	0·59
	3	0·0003	0·0326	0·0272	0·64	—	—	—
	4	0·0709	0·0960	0·1005	2·38	—	—	—
	6	0·0829	0·0938	0·0841	1·99	—	—	—
	7	0·0714	0·0756	0·0841		—	—	—
(II)	O(a)	0·0552	0·0571	—	—	—	—	—
	N(a)	0·0410	0·0373	—	—	0·29	0·40	—
	2	0·0707	0·0788	0·0785	1·86	—	—	—
	3	0·0644	0·0649	0·0650	1·54	—	—	—
(III)	O(a)	0·0474	0·0486	—	—	—	—	—
	N(a)	0·0320	0·0282	—	—	0·79	0·69	0·73
	O(b)	0·0394	0·0404	—	—	—	—	—
	N(b)	0·0266	0·0227	—	—	0·58	0·65	0·73
	O(c)	0·0360	0·0358	—	—	—	—	—
	N(c)	0·0243	0·0207	—	—	0·60	0·61	0·46
	3	0·1017	0·1012	0·0613	1·45	—	—	—
	6	0·0678	0·0768	0·0105	0·25	—	—	—
	7	0·0643	0·0689	0·0105	0·25	—	—	—
(IV)	O(a)	0·0340	0·0309	—	—	—	—	—
	N(a)	0·0237	0·0206	—	—	0·46	0·18	0·35, 0·65 [c]
	O(b)	0·0287	0·0262	—	—	—	—	—
	N(b)	0·0199	0·0164	—	—	0·35	0·25	0·35, 0·65 [c]
	3	0·0282	0·0253	0·0253	0·60	—	—	—

[a] Calculated from equation (1). [b] Calculated from equation (2). [c] Cannot be unambiguously assigned.



Since these results relate to the same solvent, *viz.* 1,2-dimethoxyethane, it is unlikely that these marked differences in couplings arise from differences in solvent-anion interactions. The absence of hyperfine coupling to nitrogen in 4,5-dinitronaphthalic anhydride still awaits an explanation.

The spectrum of the radical anion of 2,4,5-trinitronaphthalic anhydride can be explained as arising from interactions involving one individual proton, two equivalent protons, one individual nitrogen, and two equivalent nitrogen nuclei. Comparison of the experimental spectrum with the spectrum simulated on the basis of these interactions and the observed coupling constants reveals that although the line positions and the overall width of the spectra compare favourably, the

intensities of the lines differ considerably. This difference is probably due to line broadening brought about by cation migration between sites in the ion pair. Whether the cation would migrate between the *meta* nitro-groups or the *peri* nitro-groups or between all three sites is still an open question. Line broadening brought about cation migration between sites in an ion pair has been observed in the spectra of the radical anions of *o*- and *m*-dinitrobenzenes.[23] Whereas cation hyperfine splitting was observed in the spectra of the dinitrobenzene radical anions it was not observed in any of the spectra at present under discussion. Thus it is conceivable that line broadening in the spectrum of the radical anion of 2,4,5-trinitronaphthalic anhydride could arise from an intermolecular effect involving cation exchange.

The Hückel and McLachlan calculations for the 2,4,5-trinitronaphthalic anhydride indicate that the magnetically equivalent protons in this system are those *ortho* in the ring. Here, as in other systems where line-broadening effects are operative,[25] the agreement between calculated and experimental π-electron spin densities is poor. Comparison of the experimental nitrogen coupling constants with the values derived from the Hückel and McLachlan spin densities suggests the assignment given in column 9 of Table 3.

The spectrum of the radical anion of 2,4,5,7-tetranitronaphthalic anhydride does not exhibit line broadening and here the agreement between the calculated and experimental spin densities is excellent. The spectrum in this case arises from interactions involving two equivalent protons and two pairs of equivalent nitrogen nuclei. The experimental nitrogen coupling constants cannot be assigned to specific nuclei since there are large discrepancies between the calculated and experimental nitrogen coupling constants. Such discrepancies have been found for other nitroaromatic radical anions.[24]

The extent of nitrogen hyperfine interaction in the radical anions which have nitro-groups in the *peri* positions varies in an interesting manner. For the dinitro-species the nitrogen coupling is apparently zero, for the trinitro-species the coupling is finite but the line broadening associated with the nitrogen nuclei is apparent, and for the tetranitro-species the coupling is finite but no line-broadening effects are observed. It would thus appear that if nitrogen interaction and line broadening are related to cation migration then there is a wide range of migration rate in the di-, tri-, and tetranitro-series of naphthalic anhydrides.

[29] B. C. Webb, C. H. J. Wells, and J. A. Wilson, to be published.

[30] F. Bell, *J. Chem. Soc.*, 1952, 1952.

EXPERIMENTAL

The nitronaphthalic anhydrides studied were prepared either by literature methods or in the case of new compounds by methods developed in the course of the work.[29] The compounds prepared by literature methods were purified until the m.p. was equal to or higher than the reported value: 2,5-dinitronaphthalic anhydride,[29] m.p. 232—235°; 4,5-dinitronaphthalic anhydride,[30] m.p. 322° (lit., 322°); 2,4,5-trinitronaphthalic anhydride,[29] m.p. 244—245° (decomp.); and 2,4,5,7-tetranitronaphthalic anhydride,[29] m.p. 292—295° (decomp.).

The solvent, 1,2-dimethoxyethane, was dried over sodium, trap-to-trap distilled from alumina and sodium hydroxide pellets onto sodium and anthracene, and thoroughly degassed.

The radical anions were prepared as follows: the nitronaphthalic anhydride (*ca.* 2 mg) was placed in a quartz tube (4 mm o. diam.) which formed an outer limb of a three-limbed vessel. Sodium metal (*ca.* 0·5 g) was placed in the other outer limb and the vessel was evacuated. A sodium mirror was formed by gently heating the sodium and the end of the limb was sealed off to isolate any impurities. Dimethoxyethane (*ca.* 0·3 cm^3) was distilled into the central limb and degassed several times and the vessel was then sealed and removed from the vacuum line. The solvent was shaken with the sodium mirror and carefully poured onto the nitro-compound. As soon as colouration, indicative of radical anion formation, became apparent the limb was immediately immersed in liquid nitrogen and stored until the e.s.r. spectrum was recorded. The spectra was recorded at −40 °C on either a Varian E-4 or E-9 spectrometer. The spectral coupling constants were read directly from the calibrated charts.

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Dr CHJ Wells

Molecular complexes in reaction mechanisms

In a previous article in *Education in Chemistry*[1] the nature of molecular complexes between electron-donor and electron-acceptor species was discussed and some of the methods used to detect such complexes in chemical systems were considered. Molecular complexes are thought to play an important role in a wide variety of reactions, and some of these are considered.

In most systems where reaction occurs between electron-donor and electron-acceptor species it is still an open question as to whether the complexes are formed in independent side reactions or whether they are essential intermediates in the reaction. Nevertheless, there is evidence to suggest that in certain reactions molecular complexes do play a direct role in the reaction sequence. These include important processes such as electrophilic aromatic substitution (Friedel–Crafts reaction, aromatic halogenation), nucleophilic aromatic substitution and Diels–Alder reactions. Here, examples have been restricted to the reactions of amines, polymerizations and photochemical reactions. For a more extensive discussion of the role of molecular complexes in reaction mechanisms, the reader is referred to three excellent reviews.[2–4]

Reactions of amines

Many aliphatic and aromatic amines can act as electron donors and react with compounds which are electron acceptors. These reactions are often accompanied by striking colour changes, ranging through violet, blue, green, yellow, orange and red. For example, mixing chloroform solutions of *N,N*-dimethylaniline and tetracyanoethylene gives, instantaneously, a blue colour which rapidly changes to pink and then to red.[5] *Scheme 1* shows the postulated mechanism for this reaction. The initial step is the formation of a molecular complex (blue coloration) in which the components are bound by van der Waals' interaction between the π-orbitals of the donor and acceptor. This then converts to a covalently bonded complex from which the reaction proceeds.

Similar mechanisms have been suggested for the reactions of aniline and its *N*-methyl derivatives with chloranil and tetracyanoethylene.[6–8] The reaction between 1,3,5-triaminobenzene and chloranil is also similar: here it has been claimed[8] that there is direct evidence for the conversion of the molecular complex to the covalently bonded complex. The reaction of *N,N*-dimethylaniline with iodine[9] is thought to proceed *via* a mechanism in which the initially formed molecular complex is converted to a covalently bonded complex by a sequence of reactions (*Scheme 2*).

In the reaction of triethylamine with chloranil, it has been suggested[2] that the step subsequent to molecular complex formation involves electron transfer from donor to acceptor component to give two radical ions. These then react to give tetrachlorohydroquinone, and finally *N,N*-diethylaminovinyl-trichloro-*p*-benzoquinone and hydrochloric acid (*Scheme 3*).

Another reaction that may be classified as an amine–electron acceptor reaction is that of 1-ethyl-4-carbomethoxypyridinyl with *p*-nitrobenzylchloride. The rate of this reaction is extremely sensitive to the polarity of the solvent and it has been deduced from this that one step in the mechanism involves transfer of an electron, within a molecular complex, from the pyridinyl radical to *p*-nitrobenzylchloride. Since such a step will involve the formation of a highly polar species, the ease of formation of this species, and hence the reaction rate, will be markedly dependent upon the solvent system.

Polymerization

The polymerization of certain vinyl compounds can be initiated by the addition of compounds which possess electron acceptor properties. In view of this, and the fact that the π-electron system of the vinyl group will be an electron donor site, it seems likely that these polymerizations are initiated as a result of complex formation. It is proposed that the molecular complex is an intermediary in the production of the monomer radical cation which initiates the chain process.[10]

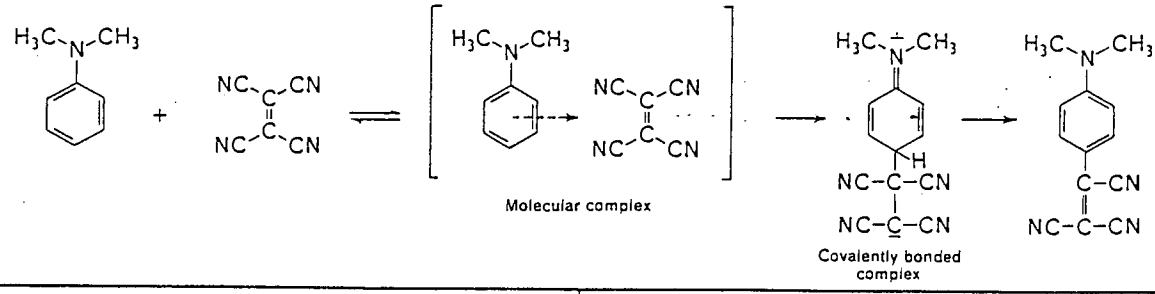
The polymerization of vinyl ethers in the presence of the tropylium ion, $C_7H_7^+$, is an example of this type of initiation.[10] The tropylium ion is a powerful electron acceptor and it is reasonable to expect that the formation of a complex between the vinyl ether and tropylium ion will lead to the donation of an electron to the ion and the consequent formation of a radical cation and tropylium radical.

$$C_7H_7^+ SbCl_6^- + CH_2{=}CHOR \rightleftharpoons [\text{Molecular complex}] \rightarrow C_7H_7 + {}^{\cdot}CH_2{-}\overset{+}{C}H = \overset{+}{O}R$$

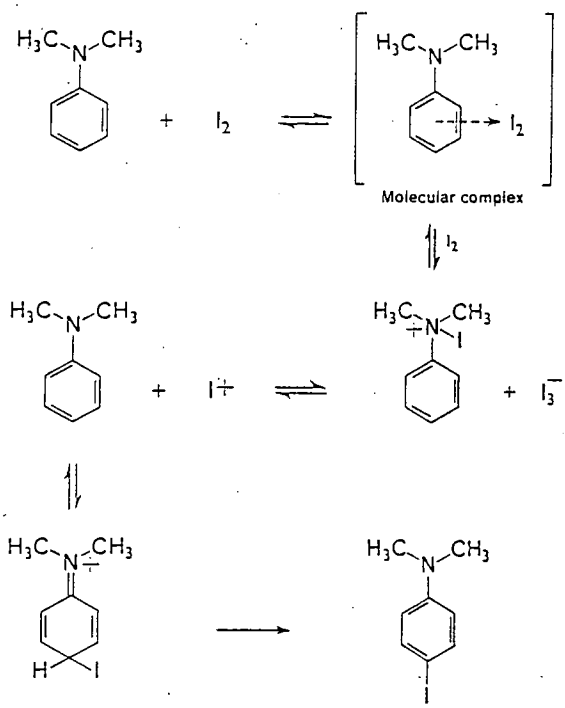
The polymerization of *N*-vinyl carbazole is also initiated by electron acceptor compounds. Features of this polymerization are that it can be initiated by a variety of electron acceptors of widely different electron affinity (acrylonitrile, chloranil, 1,3,5-trinitrobenzene, tetracyanoethylene *etc.*), and that initiation by acrylonitrile and methyl methacrylate results in almost pure homopolymer, even though these compounds readily copolymerize with *N*-vinyl carbazole in the presence of a free radical initiator. The latter observation is further indirect evidence that the polymerization results from complex formation.

The kinetics of the copolymerization of 1,2-dimethoxyethylene and of *p*-dioxane with maleic anhydride suggest that molecular complexes take part.[2] In these systems, it is thought that the molecular complexes participate

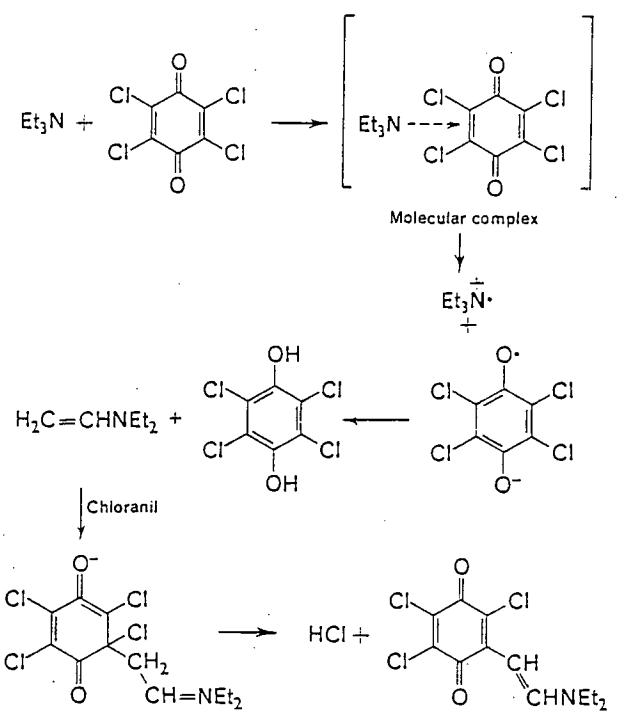
Scheme 1



Scheme 2



Scheme 3



in both the initiation and propagation steps. The possible participation of molecular complexes in the copolymerization reactions between 2,4,6-trinitrostyrene and vinylpyridines has also been considered.[12]

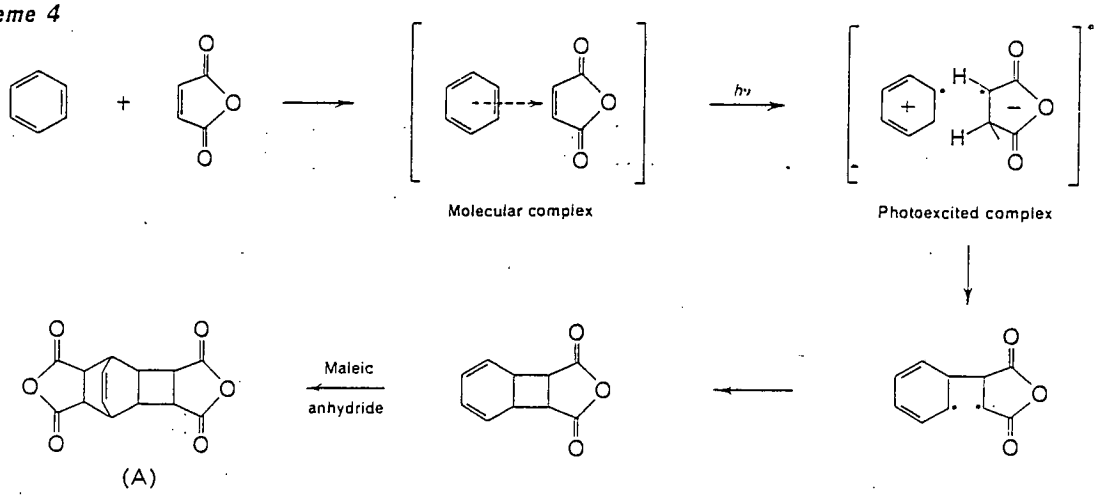
Photochemical reactions

Molecular complexes often exhibit intense absorption bands in the ultraviolet–visible region of the spectrum, and, frequently, these bands occur over a wavelength range where neither of the individual donor and acceptor components absorb. This feature is particularly useful in ascertaining whether or not a photochemical reaction proceeds *via* a molecular complex since, by appropriate choice of the incident radiation, the molecular complex can be selectively promoted to an excited state while the uncomplexed reactant molecules remain in the non-activated ground state. If, under these conditions, the products of the reaction are the same as those formed when the uncomplexed reactants are excited, or if the reactants do not give products when excited, it may be assumed that the reaction depends on the formation of the complex.

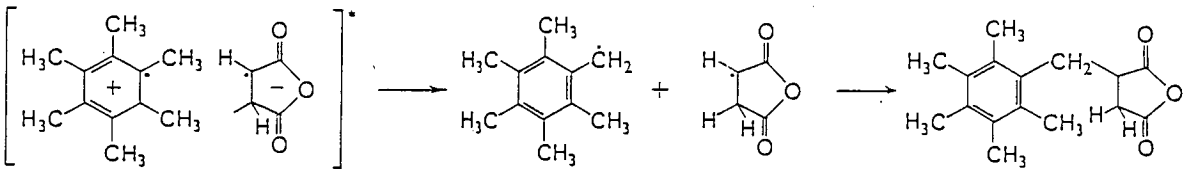
One photochemical reaction in which a molecular complex appears to play an important part is that between benzene and maleic anhydride. These compounds form a molecular complex which absorbs at longer wavelengths than either benzene or maleic anhydride, and when the system is irradiated with radiation (λ = 280–325 nm) which is only absorbed by the complex, the adduct A (*Scheme 4*) is formed.[13] Irradiation of the system under experimental conditions where only 3 per cent of the maleic anhydride was present as the complexed form gave no detectable amount of adduct A. A possible mechanism for the reaction is given in *Scheme 4*.

The absorption of radiation by the benzene–maleic anhydride complex causes the transition of an electron from a molecular orbital of the donor species to a higher energy molecular orbital of the acceptor species: this leads to the formation of a photoexcited complex which is a radical ion pair. Conversion of the radical ion pair to a diradical intermediate could then give the 1:1 benzene–maleic anhydride adduct, and subsequent 1,4-addition of a second molecule of maleic anhydride would give the adduct A. In principle, energy transfer from the photoexcited complex to uncomplexed benzene or maleic anhydride followed by reaction of the energetically excited benzene or maleic anhydride is also possible, but this is less likely to lead to A than the proposed mechanism.

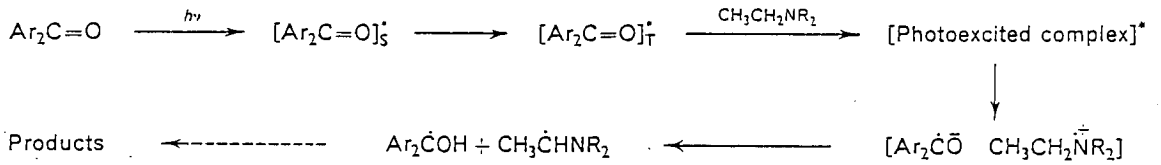
Scheme 4



Scheme 5



Scheme 6

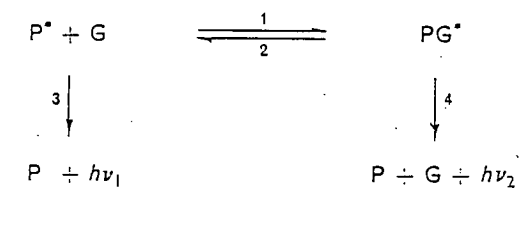


The products of photochemical reactions involving molecular complexes will depend on the mode of reaction of the components within the complex. In the last example, the components reacted to form a di-radical and the products of the reaction were readily explained in terms of subsequent reaction of this intermediate. In the reaction of hexamethylbenzene with maleic anhydride, the nature of the products indicates that the components of the complex do not form a radical but are involved in a proton-transfer reaction instead (*Scheme 5*).[14]

Photoexcited molecular complexes may be formed either by direct absorption of radiation by a molecular complex consisting of ground-state molecules, or by combination of a photoexcited molecule with a ground-state molecule. An example of the latter is the complex formed between photoexcited anthracene and ground-state triethylamine. This energetically excited complex is thought to be an intermediate in the reduction of the anthracene moiety.[15]

A photoexcited molecule which combines with a ground-state molecule to give the activated molecular complex may be in either an excited singlet state (S) or a triplet state (T). For example, the photoreaction of anthracene with triethylamine involves an excited singlet state of anthracene,[15] while, in the photo-reduction of aromatic ketones by tertiary amines, it is a triplet state of the ketone which is involved in the complex-forming step (*Scheme 6*).[16] Conversion of the photoexcited complex to a radical ion pair complex appears to be a necessary step in the mechanism leading to the products (*Scheme 6*). Both these types of intermediate complex have been postulated in the photochemical reactions of ketones with phosphites,[17] phosphines[17] and sulphides.[18]

Scheme 7



ν_1=fluorescence frequency of P*
ν_2=fluorescence frequency of PG*

Photoexcited molecules may return to the ground state by emission of radiation: if the ground and excited states are both singlet states then the emitted radiation is termed fluorescence. The formation of a molecular complex between a photoexcited molecule, P*, capable of fluorescing, and a ground-state molecule, G, can result in quenching of the fluorescence of P*.[19] This arises because the system can return to the ground state by an alternative pathway—through emission of radiation by the complex PG* (*Scheme 7*). The proportion of P* fluorescence to PG* fluorescence in the total emitted radiation is dependent upon the relative rates of the processes 1, 2, 3 and 4.

Formerly a research chemist with ICI, and now senior lecturer at Kingston Polytechnic, Dr Wells' research interests are in photochemistry, spectroscopy and charge-transfer complexes. He is co-author of Introduction to molecular spectroscopy: theory and experiment *(Academic) published last year, and a counsellor for the Open University.*

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A MEISENHEIMER COMPLEX OF 3,5,6,8-TETRANITROACENAPHTHENE

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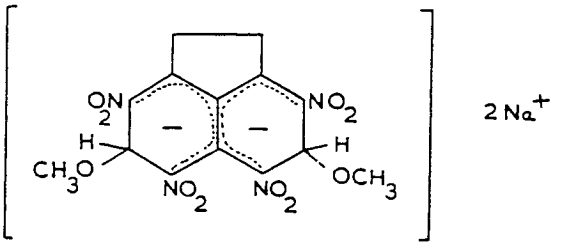
Meisenheimer complexes are formed by nucleophilic attack at electron - deficient sites in aromatic molecules and are of importance in regard to their role as intermediates in nucleophilic aromatic substitution reactions (1). The reactions of nucleophiles with polynitroaromatic compounds have been extensively studied and the results reviewed in detail (2,3). Although many 1-substituted polynitrobenzenoid compounds react with nucleophiles to give the expected Meisenheimer complexes α - trinitrotoluene is an exception and the reactions of this compound with base are more complicated due to the possibility of proton abstraction from the methyl group (4). 3,5,6,8-tetranitroacenaphthene bears a structural resemblance to α - trinitrotoluene in that it contains nitro substituents symmetrically disposed ortho and para to an aliphatic group. However, unlike α - trinitrotoluene, 3,5,6,8-tetranitroacenaphthene yields an isolatable Meisenheimer complex on reaction with methoxide ion.

Treatment of 3,5,6,8-tetranitroacenaphthene in dry dichloromethane, under a blanket of nitrogen, with sodium methoxide resulted in a bright red solution. Cooling to 0° caused the precipitation of a brown solid which was filtered off under nitrogen and identified as the Meisenheimer complex, I, shown below. (Found: C, 37.5; H, 2.4; N, 13.1; Na, 10.6. $C_{14}H_{12}N_4O_{10}Na_2$ requires C, 38.0;



(I)

H, 2.7; N, 12.7; Na, 10.4%); n.m.r. spectrum in $(CD_3)_2SO$: singlet (2H) τ3.80, singlet (4H) τ5.82, and a singlet (6H) τ6.79.

The upfield shift of the aromatic resonance representing two protons from τ0.80 in 3,5,6,8-tetranitroacenaphthene to τ3.80 in the complex indicates that the ring protons are bonded to the carbon atoms at which attack of the anion takes place (2). The resonance at τ5.82 corresponds to four protons and arises from the methylene bridge protons in the complex. The integrated intensity of this resonance and the small shift from the resonance position (τ5.83) in 3,5,6,8-tetranitroacenaphthene provides evidence that the attack of the methoxy ion occurs by substitution in the ring system and not by proton abstraction from the methylene bridge. The sharp resonance at τ6.79 representing six protons indicates that the methoxyl groups are equivalent and are in an environment which corresponds more closely to an aliphatic ether than to an aromatic ether.

An interesting feature of the Meisenheimer complex, I, is that it is stabilised by two nitro groups per negative charge whereas normally for complexes to be isolatable three nitro groups per negative charge are required. This is especially significant since steric interaction between the nitro groups at the 5- and 6- positions forces them out of the plane of the ring and diminishes the Lewis acid effect of these groups.

Structure I will be of high energy and the expected instability of complexes with this type of structure is borne out by the fact that the complex isolated from the reaction of ethoxide ion with 3,5,6,8-tetranitroacenaphthene detonated on touch.

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and C H J Wells

Visible absorption spectrum of iodine vapour

Today, an introduction to spectroscopy forms part of many A-level syllabi and there is a growing need for experiments in this field which are suitable for sixth-forms. A recent article in *Education in Chemistry* (1971, 8, 178) described the use of a relatively low-cost commercial spectrometer in experiments relating the colour and absorption spectra of first-row d-block elements. This article describes how the visible absorption spectrum of iodine vapour, obtained with the same spectrometer, can be used to demonstrate fundamental spectroscopic principles. Quantitative information on the iodine molecule can be obtained from the spectrum.

Spectroscopy is a subject which has attracted much attention in recent years because of the importance of the information it provides on the microscopic structure of matter and because of its applications in problems of analysis. It is concerned with the interaction of radiation with matter, and the different branches of the subject deal with interactions involving radiation from the different regions of the electromagnetic spectrum. Visible radiation constitutes only a small part of the entire spectrum but it was from Newton's observation that visible radiation could be dispersed into its component colours that the subject of spectroscopy originated. Newton's experiment can be demonstrated with the apparatus in *Fig. 1a*. In this arrangement, the component colours are shown up by projection on to a screen.

The selective absorption of the components of visible radiation is the basis of the phenomenon of colour. Iodine vapour owes its characteristic red–violet tint to the fact that it mainly absorbs the radiation corresponding to the orange, yellow and green parts of the spectrum, leaving the transmitted radiation relatively richer in violet, blue and red light. Thus, if a sample of iodine vapour is placed between the source and screen (*Fig. 1b*) an absorption band will be observed over the orange to green regions on the screen.

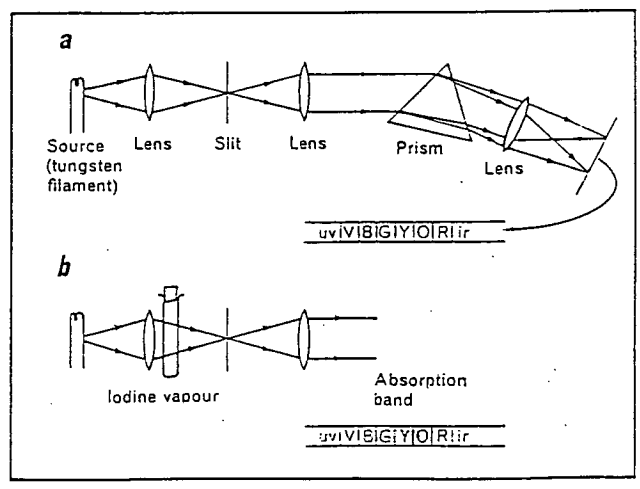
Another arrangement for obtaining the absorption spectrum is to have a slit device and photoelectric detector placed after a rotatable prism. As the prism is rotated, radiation of a narrow wavelength range passes through the slit and on to the photoelectric detector. The signal from the detector may then be amplified and fed to a galvanometer or pen recorder. When there is no sample between the source and detector the intensity of radiation of different wavelengths reaching the detector is proportional to the intensity of the source at these wavelengths and the emission spectrum of the source is recorded (*Fig. 2a*). But if a sample of iodine vapour is inserted, a band of radiation is absorbed and within this band the intensity of radiation reaching the detector is reduced. This results in a trough in the emission spectrum of the source (*Fig. 2b*). The trough represents the visible absorption spectrum of iodine vapour. With suitable instrumental operating conditions the iodine absorption band shown schematically in *Fig. 2b* is found to have detailed fine structure (*Fig. 3*).

Explanation

In order to explain the visible absorption band of iodine and its detailed fine structure, the electronic and vibrational energy states of molecules must be considered. The uptake of energy by the iodine molecule on absorption of visible radiation causes an electron to be promoted from a lower energy to a higher energy orbital with the resultant formation of an *excited* state of the molecule. Molecules in the initial state—before electronic excitation—are said to be in the *ground* state. Iodine molecules, like other molecules, are continuously vibrating and the potential energies of the ground state and excited state molecules change with the internuclear separation of the iodine atoms. Since the binding forces in the molecule, as represented by the electronic structure, are different for the two states, the change in potential energy with internuclear separation will also differ for the two states. This is represented in *Fig. 4* where the upper curve representing the state of higher energy, the excited state, is displaced to larger internuclear separations relative to the lower curve.

The energy of a molecule is made up of four types—translational, electronic, vibrational and rotational. For spectroscopy in the visible region, only the electronic and vibrational energies are significant. The electronic

Fig. 1. Apparatus and diagrammatic spectra for (a) dispersion of visible light; (b) absorption by iodine vapour.



energy of a molecule in either the ground or an excited state is the sum of the energies of the electrons in the different orbitals in these states. The vibrational energy of a molecule arises from the vibrations of atoms and, for any state, it is confined to specific values, *i.e.* it is quantized. The quantized vibrational energy levels of the iodine molecule in the ground and excited states are represented schematically by the horizontal lines on the potential energy curves of *Fig. 4*. The energy of each level is a function of an integer v which is called the vibrational quantum number.

Absorption of radiation of appropriate energy results in the formation of an excited state in which any of the vibrational levels ($v' = 0, 1, 2, \ldots$) may be populated, *i.e.* there are a large number of possible transitions, $v = 0$ to $v' = 0$, $v = 0$ to $v' = 1$, $v = 0$ to $v' = 2$ *etc.* Some of these are shown by the vertical arrowed lines in *Fig. 4*. The different transitions require the absorption of radiation of different wavelength and, in certain cases, each transition may be observed as an absorption band in the spectrum of the molecule. For the apparatus described, the transitions will be observed as troughs in the emission spectrum of the source (*Fig. 3*).

Quantitative theory

The energy required for individual transitions is the difference between the energy, $E_{v=0}$, of the lower vibrational level and the energy, $E_{v'=0,1,2\ldots}$, of the upper vibrational level. Thus, the *difference* in energy between transitions from the ground state level $v = 0$ to the excited state levels v' and $v' = n$ is the difference between the energy, $E_{v'}$ of the excited state level v' and the energy, $E_{v'+n}$, of the excited state level $v' + n$. If each trough in the emission spectrum of the source represents an individual transition, the difference in energy between transitions from the ground state to the v' and $v' + n$ levels of the excited state can be obtained, in principle, directly from the spectrum by measuring the difference in energy between the corresponding troughs.

The minimum of each trough occurs at a specific wavelength, λ, and the corresponding energy, in units of cm^{-1}, is related to the wavelength of the absorbed radiation by the expression

$$\bar{\nu} = 1/\lambda \qquad (1)$$

where $\bar{\nu}$ is the wavenumber of the radiation—the number of waves in one centimetre.

Table 1. Wavenumber values of transitions in the iodine absorption spectrum.

Transition	Wavenumber† (cm^{-1})	Transition	Wavenumber‡ (cm^{-1})	$\Delta\bar{\nu}_{10}$ (cm^{-1})
0→ 21	18 011	0→ 31	18 776	765
22	18 116	32	18 832	716
23	18 172	33	18 892	720
24	18 271	34	18 953	682
25	18 362	35	19 015	653
26	18 430	36	19 066	636
27	18 498	37	19 127	629
28	18 577	38	19 172	595
29	18 649	39	19 231	582
30	18 712	40	19 275	563

† Comparison with literature values[4] shows that these values are within + 50 cm^{-1} of true values. ‡ Comparison with literature values[4] shows that these values are within −40 cm^{-1} of true values.

The energy, $E_{v'}$, of a vibrational level in the excited state is given, to a first approximation, by

$$E_{v'} = a(v' + \tfrac{1}{2}) - ab(v' + \tfrac{1}{2})^2 \qquad (2)$$

where v' is the quantum number of the vibrational level, a is a constant with units of cm^{-1} and b is a dimensionless constant.

The difference in energy, ΔE_n, between vibrational levels of energy $E_{v'}$ and $E_{v'+n}$ is equal to $\Delta\bar{\nu}_n$ (the energy difference between the corresponding troughs) and is given by

$$\Delta E_n = \Delta\bar{\nu}_n = E_{v'+n} - E_{v'} \qquad (3)$$

Substituting the appropriate expressions for $E_{v'+n}$ and $E_{v'}$ from equation 2 into equation 3 gives

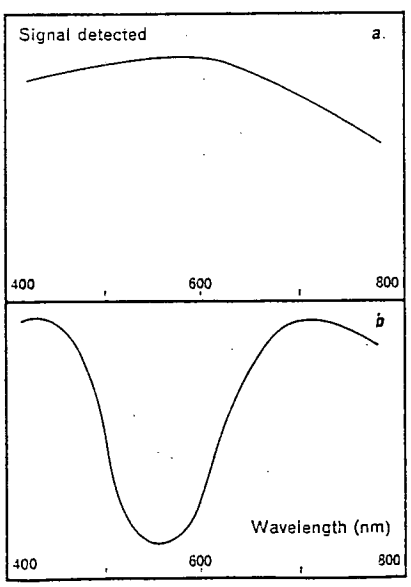
$$\Delta\bar{\nu}_n = n\,(a - (n + 1)ab) - 2nabv' \qquad (4)$$

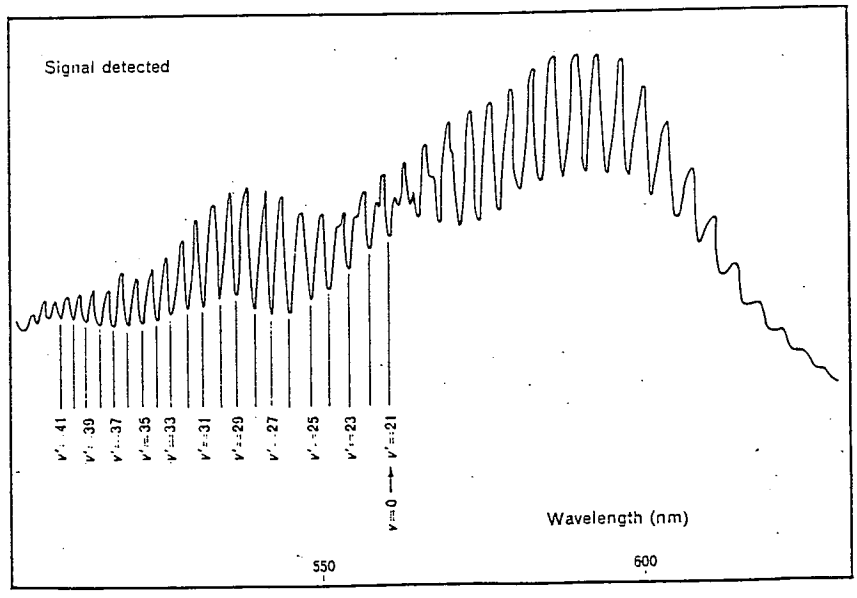
Equation 4 suggests that if measured values of $\Delta\bar{\nu}_n$ are plotted against v' a straight line will be obtained of slope $-2nab$ and with an intercept of $n(a-(n + 1)ab)$. Thus, values of a and b can be obtained from the plot and used to determine the dissociation energy of the iodine molecule in the excited state (*see below*).

If the wavelength of each trough can be measured accurately (±0.02 per cent) it is feasible to measure differences between adjacent troughs ($\Delta\bar{\nu}_1$). If, however, the wavelength can only be measured with moderate

Fig. 2. (Left) (a) Emission spectrum of the source. (b) Absorption spectrum of iodine vapour.

Fig. 3. (Below) Assignment of fine structure in the absorption spectrum of iodine vapour.





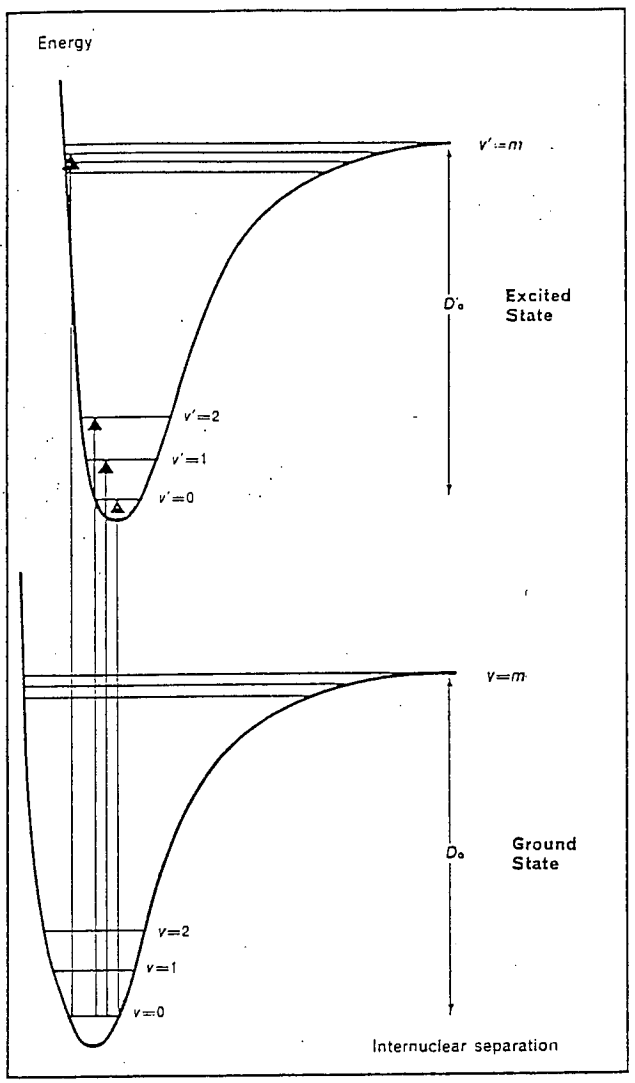


Fig. 4. Variation of potential energy with internuclear separation for the ground and excited states of a diatomic molecule such as iodine vapour. Vibrational energy levels are represented by horizontal lines.

accuracy (±0.2 per cent), a more accurate value is obtained if the differences are measured between troughs separated by, say, 10 intervals ($\Delta\bar{\nu}_{10}$). In the latter case, the appropriate equation, corresponding to equation 4, is

$$\Delta\bar{\nu}_{10} = (10a - 110ab) - 20abv' \quad (5)$$

The separation of adjacent vibrational levels in the excited state decreases as v' increases and becomes zero when $v' = m$ (*see Fig. 4*). From equation 4, the energy difference between the $v' = m$ and $v' = m-1$ levels is

$$\Delta\bar{\nu}_1 = 0 = (a - 2ab) - 2ab\,(m-1) \quad (6)$$

Thus

$$m = 1/2b \quad (7)$$

The dissociation energy, D'_0, of the iodine molecule in the excited state is the difference between the energy of the lowest vibrational level ($v' = 0$) in the excited state and that of the vibrational level ($v' = m$) in which the internuclear separation of the iodine atoms goes to infinity. Thus

$$\begin{aligned} D'_0 &= E_{v'=m} - E_{v'=0} \\ &= [a(m+\tfrac{1}{2}) - ab(m+\tfrac{1}{2})^2] - [a(\tfrac{1}{2}) - ab(\tfrac{1}{2})^2] \\ &= am - abm - abm^2 \end{aligned} \quad (8)$$

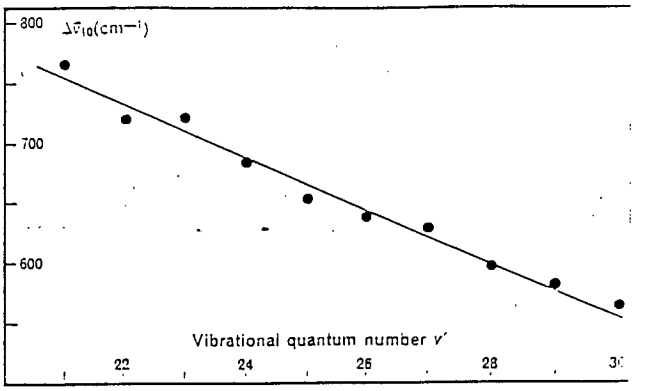


Fig. 5. Energy separation between the vibrational levels v' and $v'+10$ as a function of v'. Constants a and b are obtained from this plot.

Substituting the value for m given by equation 7 into equation 8 gives

$$D'_0 = \frac{a}{4}\left(\frac{1}{b} - 2\right) \quad (9)$$

Thus once the values of a and b are known, the dissociation energy, D'_0, can be calculated. It is also possible to derive the force constant of the I–I bond in the excited state, the convergence limit, the dissociation energy of the iodine molecule in the ground state, and the theoretical potential energy curve for the excited state molecule (*see* ref. 1).

Results

The visible absorption spectrum of iodine vapour obtained on an MLI Vuespec spectrometer[2] is shown in *Fig. 3*. The spectrum consists of three overlapping band systems;[3] at the longer wavelengths the spectrum results from overlapping transitions originating from the $v = 1$ and $v = 2$ levels of the ground state, while at the shorter wavelengths it results from transitions originating from the $v = 0$ level.

The transitions from $v = 0$ to $v' = 21$ and higher levels are marked on *Fig. 3*. The wavelengths of these transitions were determined using the manufacturer's calibration data.[2] The wavenumber values are listed in Table 1 and the plot corresponding to equation 5 is shown in *Fig. 5*. The values of a and b derived from this plot are 134.0 cm^{-1} and 8.210×10^{-3} respectively. These give the dissociation energy, D'_0, for the iodine molecule in the excited state as 48.07 kJ mol^{-1} (4015 cm^{-1}).

Acknowledgements

We should like to thank Mr W. D. Tucker for recording the iodine spectrum and providing calibration data. The late Mr K. S. Tetlow designed the Vuespec and we were grateful to him for many helpful comments.

Dr George is principal lecturer in analytical chemistry and Dr Wells senior lecturer in physical and analytical chemistry at Kingston Polytechnic. They are co-authors of Introduction to molecular spectroscopy *and Dr George edited* Spectroscopic methods in organometallic chemistry.

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Studies on Nitroaromatic Compounds. Part III.[1] The Synthesis of Some New Polynitroacenaphthenes

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Studies on Nitroaromatic Compounds. Part III.[1] The Synthesis of Some New Polynitroacenaphthenes

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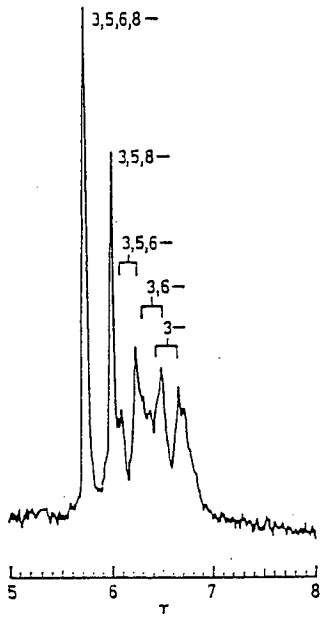
The nitration of mono- and di-nitroacenaphthenes in various media has been investigated, and it has been found that nitration occurs preferentially at the positions *para* to the aliphatic bridge. Methods have been devised for the preparation of 3,7-dinitroacenaphthene, 3,8-dinitroacenaphthene, 4,6-dinitroacenaphthene, 3,5,6-trinitroacenaphthene, 3,5,7-trinitroacenaphthene, 3,5,8-trinitroacenaphthene, 3,6,7-trinitroacenaphthene, 4,5,6-trinitroacenaphthene, 3,5,6,7-tetranitroacenaphthene, and 3,4,5,6,8-pentanitroacenaphthene.

ACENAPHTHENE can be readily nitrated, and a number of mono-, di-, and tetra-nitro-derivatives have been reported.[2-4] Mononitration yields either 5-nitroacenaphthene (VII) [5,6] or a mixture of 3-nitroacenaphthene (I) and 5-nitroacenaphthene,[7,8] depending on the reagent and reaction conditions employed. The third mononitro-isomer, 4-nitroacenaphthene (IX), is not formed to any significant extent in the nitration of acenaphthene, but it may be synthesised *via* the 5-nitro-derivative.[9,10]

Dinitration of acenaphthene and the further nitration of 3- and 5-nitroacenaphthene to dinitro-derivatives have received a good deal of attention;[2,7,11-14] much confusion existed in the literature on the structure of the dinitroacenaphthenes so prepared until the paper of Dashevskii and Malevannaya [15] was published. These workers showed that the dinitration of acenaphthene and the further nitration of 3- and 5-nitroacenaphthene by the methods reported gave only 3,6-dinitroacenaphthene (II) and 5,6-dinitroacenaphthene (VIII). They were unable to obtain 3,8-dinitroacenaphthene (III) by the earlier reported procedure of Morgan and Harrison.[2] Apart from the synthesis of 3,5,6,8-tetranitroacenaphthene (VI) [4] there are no reports on nitroacenaphthenes containing more than two nitro-groups.

One of the important factors controlling the extent of nitration in aromatic systems is the type of nitrating medium used. We have found that it is possible by using nitric acid in various solvents to take the nitration of mono- and di-nitroacenaphthenes to the di-, tri-, tetra-, or penta-nitro stages, and in this way to prepare a number of new polynitroacenaphthenes.

3-Nitroacenaphthene was converted into dinitroacenaphthenes by a mixture of nitric acid and 1,2-dichloroethane. Column chromatography of the product mixture yielded 3,6-dinitroacenaphthene and 3,8-dinitroacenaphthene. The ratio of the two isomers in the product mixture, as determined by n.m.r. spectroscopy, was *ca.* 9 : 1, respectively. Thus the insertion of a second nitro-group occurs preferentially at the position *para* to the aliphatic bridge in the ring remote from the nitro-group. Preferential substitution at the *para*-position also occurs in the nitration of acenaphthene.[16] This most probably arises because the aliphatic bridge



^{1}H N.m.r. spectrum of the product mixture from the nitration of 3-nitroacenaphthene in nitric acid–sulphuric acid after 100 min of reaction; solvent nitrobenzene

distorts the naphthalenic ring system so as to increase the C(5)–C–C(6) bond angle [17] and to expose C-6 to electrophilic attack.

If the nitration of 3-nitroacenaphthene is carried out in a mixture of nitric acid and sulphuric acid the reaction

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[13] I. Honda and M. Okazaki, *J. Soc. Org. Synth. Chem.* (*Japan*), 1950, **7**, 25.
[14] J. R. Lacher, K. Ensley, A. Tenge, and J. D. Park, *J. Org. Chem.*, 1959, **24**, 1347.
[15] M. M. Dashevskii and Z. P. Malevannaya, *Zhur. org. Khim.*, 1965, **1**, 1272.
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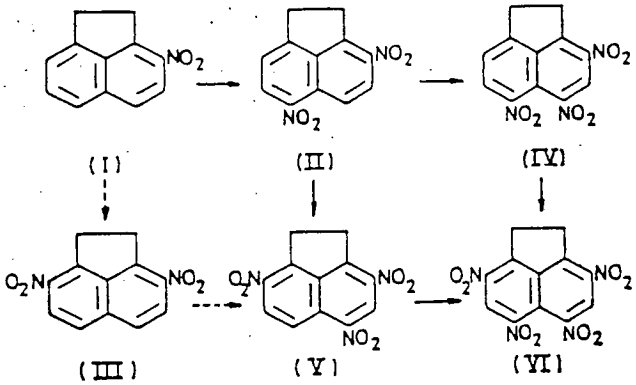
[17] H. W. W. Ehrlich, *Acta Cryst.*, 1957, **10**, 699.

proceeds through to the tetranitro stage to give 3,5,6,8-tetranitroacenaphthene. Quenching the reaction mixture in ice–water at various time intervals after the start of the nitration and comparing the n.m.r. spectrum of the precipitated product (Figure) with the n.m.r. spectra of pure samples of di-, tri-, and tetra-nitroacenaphthenes showed that the 3,5,6,8-tetranitroacenaphthene is formed by a stepwise reaction sequence involving the intermediate formation of 3,6-dinitroacenaphthene, 3,5,6-trinitroacenaphthene (IV), and 3,5,8-trinitroacenaphthene (V). The postulated steps in the nitration of 3-nitroacenaphthene in nitric acid–sulphuric acid are shown in Scheme 1.

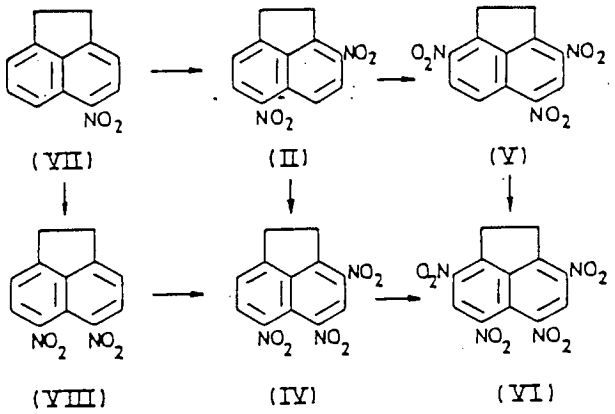


SCHEME 1

Although 3,8-dinitroacenaphthene could not be detected in the product mixture isolated from the reaction of 3-nitroacenaphthene in mixed acid, it is included as a possible reaction intermediate in Scheme 1 on the grounds that it is formed along with 3,6-dinitroacenaphthene when the nitration is carried out in nitric acid–1,2-dichloroethane.

The step in Scheme 1 involving the conversion of 3,6-dinitroacenaphthene into 3,5,6-trinitroacenaphthene and 3,5,8-trinitroacenaphthene was investigated by nitrating the 3,6-derivative in a mixture of fuming nitric acid and nitromethane. Under these conditions nitration of the trinitro-species is sufficiently slow to allow them to be isolated. The 3,5,6- and 3,5,8-trinitroacenaphthenes are formed in the ratio 7 : 3, respectively. Comparison of these figures with those for the conversion of 3-nitroacenaphthene into 3,6-dinitroacenaphthene and 3,8-dinitroacenaphthene (ratio 9 : 1) reveals that the presence of the nitro-group at the 6-position in the 3,6-dinitro-compound reduces the probability of substitution at the position *para* to the bridge relative to that for substitution at the *ortho*-position. This is probably partly owing to the steric effect of the nitro-group in the 6-position.

The course of the nitration of 5-nitroacenaphthene in nitric acid–sulphuric acid was followed, like that of 3-nitroacenaphthene, by using n.m.r. spectroscopy to analyse product mixtures isolated at different times during the reaction. The nitration proceeded *via* 3,6- and 5,6-dinitroacenaphthene and 3,5,6- and 3,5,8-trinitroacenaphthene, and gave 3,5,6,8-tetranitroacenaphthene as the final product. The probable steps in the reaction sequence are given in Scheme 2.



SCHEME 2

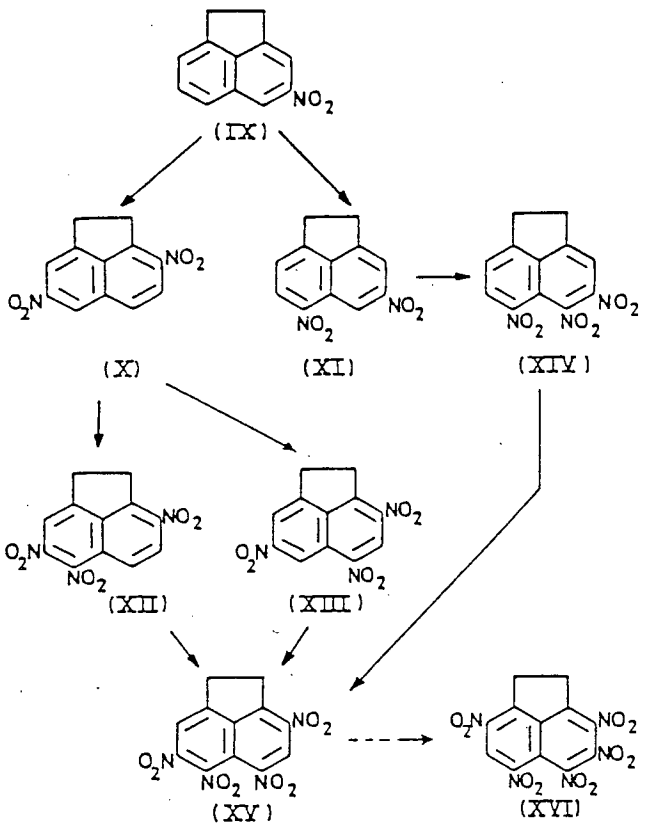
The initial nitration step of Scheme 2 produces the previously characterised 3,6- and 5,6-dinitroacenaphthenes. Further nitration of these dinitroacenaphthenes to the corresponding trinitroacenaphthenes can be studied by use of nitric acid–nitromethane as the nitration medium. Nitration of 3,6-dinitroacenaphthene gave 3,5,6- and 3,5,8-trinitroacenaphthene (see before); nitration of 5,6-dinitroacenaphthene yielded 3,5,6-trinitroacenaphthene.

Polynitroacenaphthenes with a nitro-group *meta* to the aliphatic bridge can be synthesised through the nitration of 4-nitroacenaphthene. The nitration of this compound in nitric acid–acetic anhydride gave a mixture of 3,7-dinitroacenaphthene (X) and 4,6-dinitroacenaphthene (XI) in the ratio 35 : 65, respectively. These figures are similar to those for the formation of 3-nitroacenaphthene and 5-nitroacenaphthene (34 : 66) from the nitration of acenaphthene in nitric acid–acetic anhydride.[16] It thus appears that the presence of a nitro-group *meta* to the aliphatic bridge does not significantly affect the relative reactivities of the *ortho*- and *para*-sites in the unsubstituted ring. However, as would be expected, the presence of a nitro-group at the *meta*-position deactivates the *ortho*- and *para*-positions in the substituted ring towards electrophilic attack, and neither the 3,4- or 4,5-dinitroacenaphthenes could be detected in the nitration of 4-nitroacenaphthene in nitric acid–acetic anhydride.

Carrying out the nitration of 4-nitroacenaphthene in a mixture of nitric acid, sulphuric acid, and nitromethane enables the reaction to be taken through to the trinitro stage. The only product which could be isolated, however, was 4,5,6-trinitroacenaphthene (XIV); either the other possible trinitro-isomers were not formed or else they were present in low concentration in the product mixture. This indicates that the preferred route for the nitration of 4-nitroacenaphthene in nitric acid–sulphuric acid–nitromethane is 4-nitroacenaphthene ⟶ 4,6-dinitroacenaphthene ⟶ 4,5,6-trinitroacenaphthene.

The occurrence of the first step in this sequence is supported by the observation that 4,6-dinitroacenaphthene is the predominant isomer formed during the nitration of 4-nitroacenaphthene in nitric acid–acetic anhydride.

The apparent absence of both the 3,4,6- and 3,5,7-trinitro-isomers from the product mixture obtained from the nitration of 4,6-dinitroacenaphthene in mixed acid–nitromethane indicates that the position *para* to the aliphatic bridge in this compound is much more susceptible to electrophilic substitution than either of the two *ortho* sites. The predominance of *para*-substitution is also demonstrated in the nitration of 3,7-dinitroacenaphthene. Nitration of this derivative in nitric acid–sulphuric acid gave a 1 : 1 mixture of 3,5,7-trinitroacenaphthene (XIII) and 3,6,7-trinitroacenaphthene (XII). The absence of 3,4,8-trinitroacenaphthene from the product indicates that *ortho*-substitution does not occur to any significant extent. Likewise, *ortho*-substitution does not occur in the nitration of 4,6-dinitroacenaphthene in nitric acid–sulphuric acid, and 4,5,6-trinitroacenaphthene is the only detectable product.



SCHEME 3

Treatment of 4-nitroacenaphthene with excess of nitric acid in sulphuric acid at room temperature affords 3,5,6,7-tetranitroacenaphthene (XV) as the sole product. The fact that the position which is *ortho* to the aliphatic bridge and *ortho* to the *meta*-nitro-group is vacant in this product indicates that compounds (XII), (XIII), and (XIV) are likely trinitro precursors. This, taken in conjunction with the prior observations on the nitrations of the 4-nitroacenaphthene, 3,7-dinitroacenaphthene, and 4,6-dinitroacenaphthene, suggests that the nitration steps leading to the formation of 3,5,6,7-tetranitroacenaphthene are as shown in Scheme 3.

3,4,5,6,8-Pentanitroacenaphthene (XVI) can be synthesised by treating 4-nitroacenaphthene with a mixture of fuming nitric acid and sulphuric acid at 35° for 5 days. Undoubtedly the pentanitro-derivative is formed in a stepwise process involving the intermediate formation of di-, tri-, and tetra-nitro species with the final step presumably being the conversion of 3,5,6,7-tetranitroacenaphthene into 3,4,5,6,8-pentanitroacenaphthene as shown in Scheme 3.

EXPERIMENTAL

Column chromatography was carried out with Merck Kieselgel (0·05—0·2 mm) unless otherwise stated. Mass spectral molecular weights were determined with an A.E.I. MS9 spectrometer. N.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer (tetramethylsilane as internal reference). The structures of the nitration products were assigned from the n.m.r. spectra. In particular, the structures of the isomeric products were assigned by use of the following criteria: (*a*) a single nitro-group *ortho* to the aliphatic bridge resulted in an A_2B_2 pattern for the resonance of the bridge protons, (*b*) nitro-groups in the 4- and 5-positions only affected the resonance position of the bridge protons and not the resonance pattern, and (*c*) the coupling constants for *ortho*-protons in the aromatic system lay in the range 8—10 Hz while those for *meta*-protons lay in the range 0—2 Hz.

Nitration of 3-Nitroacenaphthene.—3-Nitroacenaphthene[15] was recrystallised from acetic acid and then washed with water, methanol, and ether, and dried *in vacuo*. The n.m.r. spectrum of the product in nitrobenzene showed it to be free of the 5-isomer.

(a) *In nitric acid–1,2-dichloroethane.* Nitric acid (*d* 1·42; 3·5 ml) was added with stirring to a solution of 3-nitroacenaphthene (5 g) in 1,2-dichloroethane (16 ml) so that the temperature did not exceed 40°. After 5 min, more nitric acid (3·5 ml) was added with stirring, again with the temperature kept below 40°. After a further 12 h the resulting precipitate was filtered off, washed with a small quantity of cold 1,2-dichloroethane, then with water, and dried at 70° *in vacuo*. A portion of the mixture was chromatographed on a column (500 × 20 mm) of silica gel. Initially the eluant was 1 : 8 benzene–light petroleum (b.p. 60—80°), but its composition was gradually altered during 10 days to 1 : 4 benzene–light petroleum. Fractions containing each of the three yellow bands were evaporated to dryness. The first two components were identified as 3-nitroacenaphthene and 3,6-dinitroacenaphthene by comparison of their n.m.r. spectra (CD_3NO_2) with those of authentic samples. The third component was 3,8-*dinitroacenaphthene*, m.p. 186° (Found: C, 59·1; H, 3·3; N, 11·4. $C_{12}H_8N_2O_4$ requires C, 59·0; H, 3·3; N, 11·5%); τ (CD_3NO_2) 1·58 and 2·03 (2H, ABq, J_{AB} 10 Hz) and 6·06 (4H, s); *m/e* 244 (M^+).

(b) *In nitric acid–sulphuric acid (preparative run).* 3-Nitroacenaphthene (2·0 g) was added in portions to a mixture of nitric acid (*d* 1·42; 5·0 ml), sulphuric acid

(*d* 1·84; 15 ml). After 2 h the mixture was poured on crushed ice (50 g) and stirred for 15 min. The precipitated solid was filtered off, washed with water, until the filtrate was neutral, dried *in vacuo*, and recrystallised from nitromethane to give 3,5,6,8-*tetranitroacenaphthene* (2·8 g, 85%), m.p. 213° (lit.,[4] 212°), τ (CD_3NO_2) τ 0·75(s) and 5·77(s); *m/e* 334 (M^+).

(c) *In nitric acid–sulphuric acid* (*identification run*). 3-Nitroacenaphthene (0·5 g) was added in portions to a mixture of nitric acid (*d* 1·42; 1·75 ml), sulphuric acid (*d* 1·84; 7·5 ml), and water (0·75 ml). When addition was complete one third of the total volume was withdrawn, poured on crushed ice and stirred; the resulting precipitate was filtered off, washed, and dried. Half of the remaining volume was removed after 30 min and treated likewise, and the remaining mixture was treated similarly after 100 min. The n.m.r. spectra of the solid products in nitrobenzene were recorded over the range τ 5—10 (see Figure).

Nitration of 3,6-*Dinitroacenaphthene*.[15]—(a) *In nitric acid–nitromethane*. 3,6-Dinitroacenaphthene (1·2 g) was added to a stirred mixture of nitric acid (*d* 1·5; 6 ml) and nitromethane (10 ml). After 3 days the mixture was poured on crushed ice (50 g) and stirred vigorously for 2 h. The precipitate was filtered off, washed with water, and dried *in vacuo* at 90° to give a buff-coloured solid (1·32 g). The product (0·4 g) was chromatographed on a column of silica gel (20 × 400 mm; Hopkin and Williams silica gel M.F.C.). Decomposition occurred on the column but elution with benzene at *ca.* 3 ml min^{-1} separated two yellow bands. Evaporation of the first fraction to small volume and addition of excess of light petroleum (b.p. 40—60°) gave 3,5,8-*trinitroacenaphthene* (0·06 g, 17%), m.p. 152—155° (Found: C, 50·4; H, 2·8; N, 14·4. $C_{12}H_7N_3O_6$ requires C, 49·9; H, 2·5; N, 14·5%); τ (CD_3NO_2) 0·60 (1H, s), 1·20 (2H, s, splits into an AB system on addition of benzene), and 5·86 (4H, s); *m/e* 289 (M^+).

Evaporation of the second fraction to small volume and addition of excess of light petroleum (b.p. 40—60°) gave 3,5,6-*trinitroacenaphthene* (0·05 g, 14%), m.p. 202° (Found: C, 50·0; H, 2·9; N, 14·5. $C_{12}H_7N_3O_6$ requires C, 49·9; H, 2·5; N, 14·5%); τ (CD_3NO_2) 0·92 (1H, s), 1·39 and 2·07 (2H, ABq, J_{AB} 8 Hz), and 5·88 and 6·25 (4H, A_2B_2m); *m/e* 289 (M^+).

The n.m.r. spectrum of a sample of the product mixture in nitrobenzene showed that 3,5,6-trinitroacenaphthene and 3,5,8-trinitroacenaphthene were present in the ratio 7 : 3.

Nitration of 5-*Nitroacenaphthene*.[10]—Nitration of 5-nitroacenaphthene by the method of Vernon and Wilson [4] gave 3,5,6,8-tetranitroacenaphthene.

(a) *In nitric acid–sulphuric acid* (*identification run*). 5-Nitroacenaphthene (0·5 g) was added to a mixture of nitric acid (*d* 1·42; 1·75 ml), sulphuric acid (*d* 1·84; 7·5 ml), and water (0·75 ml). When addition was complete one third of the total volume was withdrawn, poured on crushed ice, and stirred; the resulting precipitate was filtered off, washed, and dried. Half of the remaining volume of the reaction mixture was removed after 30 min and treated likewise; the remaining mixture was treated similarly after 100 min. The n.m.r. spectra of the product mixtures in nitrobenzene showed the presence of di-, tri-, and tetranitroacenaphthenes (*cf.* Figure).

Nitration of 5,6-*Dinitroacenaphthene*.[15]—(a) *In nitric acid–nitromethane*. 5,6-Dinitroacenaphthene (24 g) was added to a stirred mixture of nitric acid (*d* 1·42; 200 ml) and nitromethane (200 ml). The mixture was stirred at room temperature for 5 days then poured on crushed ice (200 g) and stirred for 2 h. The precipitate was filtered off, washed with water, and dried *in vacuo* at 90°. Recrystallisation from 1 : 1 nitromethane–glacial acetic acid gave 3,5,6-trinitroacenaphthene (20·3 g), m.p. 199° (Found: C, 49·8; H, 2·4; N, 14·3. Calc. for $C_{12}H_7N_3O_6$: C, 49·9; H, 2·5; N, 14·5%), identical (n.m.r. and mass spectra) with the sample produced in nitration of 3,6-dinitroacenaphthene in nitric acid–nitromethane.

Nitration of 4-*Nitroacenaphthene*.[10]—(a) *In nitric acid–acetic anhydride*. 4-Nitroacenaphthene (4 g) was suspended in acetic anhydride (150 ml) by vigorous stirring and cooled to −10° in an ice–salt bath. An ice-cold solution of nitric acid (*d* 1·5; 2·5 ml) in acetic anhydride (40 ml) was added dropwise during 30 min, and the mixture was then maintained at 10—20° for 3 days. It was then poured into distilled water (1 l) and the precipitated product was filtered off, washed with water, and dried *in vacuo* at 90° to give a yellow solid (3·85 g). The product (0·1 g) was chromatographed on a column of silica gel (20 × 400 mm) with 1 : 1 diethyl ether–benzene as eluant and an elution rate of 0·7—0·8 ml min^{-1}. The product separated into two yellow bands. Evaporation of the first fraction to small volume and addition of excess of light petroleum (b.p. 40—60°) gave 3,7-*dinitroacenaphthene*, m.p. 275° (Found: C, 58·5; H, 3·5; N, 11·2. $C_{12}H_8N_2O_4$ requires C, 59·1; H, 3·4; N, 11·5%); τ (CD_3NO_2) 1·28 and 1·78 (2H, ABq, J_{AB} 2 Hz), 1·67 and 1·96 (2H, ABq, J_{AB} 9 Hz), and 6·04 and 6·35 (4H, A_2B_2m); *m/e* 244 (M^+).

Evaporation of the second fraction to small volume and addition of excess of petroleum (b.p. 40—60°) gave 4,6-*dinitroacenaphthene*, m.p. 200—202° (Found: C, 58·7; H, 3·7; N, 11·3. $C_{12}H_8N_2O_4$ requires C, 59·1; H, 3·4; N, 11·5%); τ (CD_3NO_2) 0·61 and 1·80 (2H, ABq, J_{AB} 2 Hz), 1·33 and 2·24 (2H, ABq, J_{AB} 8 Hz), and 6·40 (4H, s); *m/e* 244 (M^+).

The n.m.r. spectrum of a sample of the crude product in nitrobenzene showed that 3,7-dinitroacenaphthene and 4,6-dinitroacenaphthene were present in the ratio 35 : 65.

(b) *In nitric acid–sulphuric acid–nitromethane*. 4-Nitroacenaphthene (1 g) was dissolved in nitromethane (40 ml) and nitric acid (*d* 1·5; 8 ml) was added, followed by sulphuric acid (*d* 1·84; 4 ml). The mixture was stirred for 3 h and then washed with saturated aqueous magnesium nitrate (4 × 50 ml). The nitromethane solution was then dried ($MgSO_4$) for 24 h and filtered. The clear filtrate was then reduced in volume to (*ca.* 10 ml) and stored at −10° for 6 days. The precipitated crystalline solid was filtered off, washed with dichloromethane, and dried *in vacuo*. Recrystallisation from nitromethane gave the pale yellow 4,5,6-*trinitroacenaphthene* (0·3 g, 24%), m.p. 199° (Found: C, 49·4; H, 2·9; N, 14·4. $C_{12}H_7N_3O_6$ requires C, 49·9; H, 2·5; N, 14·5%), τ (CD_3NO_2) 0·90 (1H, s), 1·17 and 2·10 (2H, ABq, J_{AB} 9 Hz), and 6·20br (4H, s); *m/e* 289 (M^+).

(c) *In nitric acid–sulphuric acid*. 4-Nitroacenaphthene (1 g) was added in portions to a stirred mixture of nitric acid (*d* 1·42; 10 ml) and sulphuric acid (*d* 1·84; 10 ml). The solution was stirred for 8 h and then poured on crushed ice (50 g). The precipitate was filtered off, washed with water, and dried *in vacuo* at 90° to give 3,5,6,7-*tetranitroacenaphthene* (1·3 g, 77%), m.p. 157° (Found: C, 43·0; H, 2·1; N, 16·8. $C_{12}H_6N_4O_8$ requires C, 43·1; H, 1·8; N, 16·8%); τ (CD_3NO_2) 0·50 (1H, s), 0·75 (1H, s), and 5·79 and 5·99 (4H, A_2B_2m); *m/e* 334 (M^+).

(d) *In nitric acid–sulphuric acid at elevated temperature*.

4-Nitroacenaphthene (0·5 g) was added in small portions to a stirred mixture of nitric acid (*d* 1·5; 10 ml) and sulphuric acid (*d* 1·84; 10 ml) maintained in an ice-bath so as to keep the temperature below 10°. The mixture was then transferred to a dried flask (50 ml) equipped with a nitrogen inlet and drying tube, and was maintained at 35° under nitrogen for 5 days. (*N.B.* If the solution is left too long, oxidation products also precipitate out.) The crystalline precipitate was filtered off, washed with water, and dried *in vacuo* to give 3,4,5,6,8-*pentanitroacenaphthene* (0·25 g, 26%) (Found: C, 37·8; H, 1·8; N, 18·6. $C_{12}H_5N_5O_{10}$ requires C, 38·0; H, 1·3; N, 18·5%); τ (CD_3NO_2) 0·61 (1H, s) and 5·77 (4H, s); *m/e* 379 (M^+).

Nitration of 3,7-Dinitroacenaphthene in Nitric Acid–Sulphuric Acid.—A mixture of nitric acid (*d* 1·5; 0·1 ml) and sulphuric acid (*d* 1·84; 25 ml) was prepared, and a portion (2·5 ml) was added to a solution of 3,7-dinitroacenaphthene (0·06 g) in sulphuric acid (*d* 1·84; 2·5 ml). The mixture was stirred for 20 h and then poured on crushed ice (15 g). The precipitate was filtered off, washed with water, and dried *in vacuo* at 45° to give an ochre-coloured product (0·05 g). All attempts to separate the mixture by column chromatography failed on account of the rapid decomposition of the products on the various stationary phases used. Elemental analysis showed that the product was a mixture of trinitroacenaphthenes (Found: C, 50·4; H, 2·5. Calc. for $C_{12}H_7N_3O_6$: C, 49·9; H, 2·5%).

The n.m.r. spectrum of a sample of the product in [$^2H_3$]-nitromethane showed that it was a 1 : 1 mixture of 3,5,7-trinitroacenaphthene (XIII) and 3,6,7-trinitroacenaphthene (XII): τ (XIII) 0·59 (1H, s), 1·46 (2H, s), and 5·90 and 6·14 (4H, A_2B_2m) (the singlet at τ 1·46 splits into a doublet on addition of C_6D_6); τ (XII) 0·47 (1H, s), 1·33 and 1·74 (2H, ABq), and 5·90 and 6·14 (4H, A_2B_2m).

Nitration of 4,6-Dinitroacenaphthene in Nitric Acid–Sulphuric Acid.—A solution of nitric acid (*d* 1·5; 0·1 ml) and sulphuric acid (*d* 1·84; 25 ml) was prepared, and a portion (2·5 ml) was added to a solution of 4,6-dinitroacenaphthene (0·06 g) in sulphuric acid (*d* 1·84; 2·5 ml). The mixture was stirred for 24 h and then poured on crushed ice (20 g). The precipitate was filtered off, washed with water, and dried *in vacuo* at 45° to give 4,5,6-trinitroacenaphthene (0·04 g), identical (n.m.r. and mass spectra) with the sample produced from nitration of 4-nitroacenaphthene in nitric acid–sulphuric acid–nitromethane.

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Studies on Nitroaromatic Compounds. Part IV.[1] Electron Acceptor Properties of Polynitronaphthalene-1,8-dicarboxylic Anhydrides in Complex Formation

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Studies on Nitroaromatic Compounds. Part IV.[1] Electron Acceptor Properties of Polynitronaphthalene-1,8-dicarboxylic Anhydrides in Complex Formation

By C. H. J. Wells * and J. A. Wilson, School of Chemical Science and Technology, Kingston Polytechnic, Kingston upon Thames, Surrey

The charge-transfer complex formation of polynitronaphthalene-1,8-dicarboxylic anhydrides with a number of aromatic hydrocarbons has been investigated. The electron affinities of the nitronaphthalenecarboxylic anhydrides have been estimated from the charge-transfer transition energy in the complexes. Thermodynamic and other data has been obtained for the complex formed between pyrene and 3,6-dinitronaphthalene-1,8-dicarboxylic anhydride.

ANHYDRIDE and nitro-groupings are electron-withdrawing entities and when bonded to atoms in a π-electron system cause an electron deficiency in the π-system. The electron acceptor properties of 3-nitronaphthalenedicarboxylic anhydride have been reported [2,3] but apart from this work the combined effects of anhydride and nitro-groups on the charge density in the naphthalenic π-electron system has not been studied. Results now obtained on the electron acceptor properties of 2,5-dinitronaphthalenedicarboxylic anhydride, 3,6-dinitronaphthalenedicarboxylic anhydride, 4,5-dinitronaphthalenedicarboxylic anhydride and 2,4,5-trinitronaphthalenedicarboxylic anhydride are reported herein.

TABLE 1

The charge-transfer maxima ($\lambda_{max.}$, nm) [a] and the energy of charge-transfer (E_{CT}, J mol^{-1} × 10^5) for a series of donor–acceptor complexes in the solid state and in chloroform solution

Donor \ Acceptor		Solid state 3,6- [b]	4,5-	2,4,5-	TNB [c]	Solution 2,5-	3,6-	TNB
Naphthalene	$\lambda_{max.}$	— [d]	445	460	400	420	—	370
	E_{CT}		2·69	2·60	2·99	2·85		3·23
Phenanthrene	$\lambda_{max.}$	—	450	470	410	420	—	370
	E_{CT}		2·66	2·54	2·92	2·85		3·23
Chrysene	$\lambda_{max.}$	450	+ [e]	+	450	460	460	420
	E_{CT}	2·66			2·66	2·60	2·60	2·85
1,2,5,6-Dibenzanthracene	$\lambda_{max.}$	470	+	+	450	500	490	430
	E_{CT}	2·54			2·66	2·39	2·44	2·78
1,2-Benzanthracene	$\lambda_{max.}$	470	+	+	460	520	510	440
	E_{CT}	2·54			2·60	2·30	2·34	2·72
Pyrene	$\lambda_{max.}$	490	550	570	475	520	510	445
	E_{CT}	2·44	2·17	2·10	2·52	2·30	2·34	2·69
Anthracene	$\lambda_{max.}$	500	560	600	490	525	525	460
	E_{CT}	2·39	2·14	1·99	2·44	2·28	2·28	2·60
3,4-Benzopyrene	$\lambda_{max.}$	550	610	640	520	570	570	475
	E_{CT}	2·17	1·96	1·87	2·30	2·10	2·10	2·52
Perylene	$\lambda_{max.}$	570	620	670	530	600	600	480
	E_{CT}	2·10	1·93	1·78	2·26	1·99	1·99	2·49

[a] Estimated accuracy is ±5 nm. [b] 3,6-Dinitronaphthalenedicarboxylic anhydride. [c] 1,3,5-Trinitrobenzene. [d] Peak minimum could not be observed. [e] Complex not formed.

RESULTS AND DISCUSSION

The wavelengths of the absorption maxima for the charge-transfer complexes formed between polynitronaphthalene-1,8-dicarboxylic anhydrides and aromatic hydrocarbons in the solid state and in chloroform solution are given in Table 1. The values for the corresponding complexes formed with 1,3,5-trinitrobenzene are included in the Table for comparison. These values are in good agreement with previously reported values.[4-7]

An interesting feature of the results given in Table 1 is that whereas the wavelength values for the complexes formed with 1,3,5-trinitrobenzene increase in going from solution to the solid state the values for the complexes formed with 3,6-dinitronaphthalenedicarboxylic anhydride decrease. It is to be noted that the intermolecular separation of the components in a charge-transfer complex can alter on changing phase and that this can contribute to a change in the energy

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of the charge-transfer transition.[8-12] It is thus feasible that the difference in the energy changes for the charge-transfer transition in the 1,3,5-trinitrobenzene and 3,6-dinitronaphthalenedicarboxylic anhydride complexes on changing phase is related to a difference in the relative separations of the components in the two types of complex. A complex can only be formed if the donor and acceptor species approach sufficiently close to each other and in this respect it is significant that solid state complexes could not be prepared between chrysene, 1,2,5,6-dibenzanthracene, and 1,2-benzanthracene as donors and 4,5-dinitronaphthalenedicarboxylic anhydride and 2,4,5-trinitronaphthalenedicarboxylic anhydride as acceptors. These particular acceptors have nitro-groups in the *peri*-positions of the naphthalene ring and because of mutual interaction between the nitro-groups they will be twisted out of the plane of the ring. Consequently the approach of the donor to the acceptor will be sterically hindered and in the case of large donor molecules the interaction may be sufficient to prevent the components taking up positions which would give stable complexes.

The electron affinities of the nitronaphthalenedicarboxylic anhydrides studied herein were calculated from the data of Table 1 using the methods of Briegleb.[13] The mean of the electron affinity values show an increasing trend in the order 3,6-dinitronaphthalenedicarboxylic anhydride ($0{\cdot}94 \times 10^5$ J mol^{-1}), 2,5-dinitronaphthalenedicarboxylic anhydride ($1{\cdot}05 \times 10^5$ J mol^{-1}), 4,5-dinitronaphthalenedicarboxylic anhydride ($1{\cdot}13 \times 10^5$ J mol^{-1}), and 2,4,5-trinitronaphthalenedicarboxylic anhydride ($1{\cdot}31 \times 10^5$ J mol^{-1}). This order can be rationalised if the effects of nitro-group substitution are additive and if substitution of a nitro-group into the positions *ortho*, *meta*, or *para* to the anhydride group has differing effects on the charge density in the π-electron system, *meta*-substitution having the least effect and *para*-substitution the greatest effect.

Electron-acceptor properties can also be evaluated from measurements of the association constants for complex formation and from measurements of the enthalpies of formation of complexes. This approach to the determination of electron acceptor ability was limited in the present study to 3,6-dinitronaphthalenedicarboxylic anhydride because of the low solubility of the other nitronaphthalenedicarboxylic anhydrides. The thermodynamic parameters evaluated for the pyrene-3,6-dinitronaphthalenedicarboxylic anhydride are given in Table 2.

The values for the enthalpy of formation of the pyrene-3,6-dinitronaphthalenedicarboxylic anhydride complex and for the oscillator strength and transition dipole moment of the charge-transfer transition are comparable to values reported for other π,π complexes.[15,16] The π,π complexing power of 3,6-dinitronaphthalenedicarboxylic anhydride will be similar to that of the 2,5-, 4,5-, and 2,4,5-nitronaphthalenedicarboxylic anhydrides and comparison of their electron affinities with other reported values [13] shows that the π,π-complexing ability of the polynitro-1,8-naphthalenedicarboxylic anhydrides is similar to that of the 2,4,7-trinitro-9-fluorenone.

TABLE 2

Association constant (K_c^{AD}), enthalpy of formation (ΔH), oscillator strength (f), and transition dipole moment (μ^2) for the 3,6-dinitronaphthalenedicarboxylic anhydride–pyrene in chloroform solution

Temp. (°C)	(K_c^{AD}) [a] (cm^3 mol^{-1})	$(-\Delta H)$ [b] (J mol^{-1} × 10^4)	(f) [c]	(μ^2) [c] (D)
2·9	$9{\cdot}56 \pm 0{\cdot}25$	$3{\cdot}1 \pm 0{\cdot}2$	0·14	19·04
27·5	$3{\cdot}27 \pm 0{\cdot}10$			
41·0	$1{\cdot}73 \pm 0{\cdot}07$			

[a] Calculated using the method given in ref. 14. [b] Calculated from the plot of log K_c^{AD} *versus* reciprocal of temperature. [c] Calculated from the equations given in ref. 15.

EXPERIMENTAL

3,6-Dinitronaphthalenedicarboxylic anhydride and 4,5-dinitronaphthalenedicarboxylic anhydride were prepared by literature methods.[17] 2,5-Dinitronaphthalenedicarboxylic anhydride and 2,4,5-trinitronaphthalenedicarboxylic anhydride were prepared by methods to be reported elsewhere.[18]

The solid complexes were prepared by mixing a solution of the nitronaphthalenedicarboxylic anhydride in hot acetic anhydride with a solution of an equimolar quantity of the donor in hot chloroform. The mixture was allowed to cool and the solid which precipitated was filtered off, washed with light petroleum (b.p. 40—60°), and dried at room temperature *in vacuo*. Elemental analysis confirmed that in each case the stoicheiometry of the complex was 1 : 1. The visible absorption spectra of the solid complexes were recorded on a Unicam SP 800 spectrophotometer fitted with a diffuse-reflectance attachment.

Complexes were prepared in solution by mixing chloroform solutions of equimolar concentration in donor and acceptor. The visible absorption spectra of the complexes were recorded on a Unicam SP 800 spectrophotometer using 40 mm cells and with a solution of the acceptor in the reference beam of the same concentration as in the sample beam.

The measurements for the determination of the association constants were taken on a Unicam SP 500 spectrophotometer fitted with a thermostat system accurate to within ±0·1°. Stock solutions of pyrene and 3,6-dinitronaphthalenedicarboxylic anhydride in chloroform were prepared just prior to use. Solutions were made up for

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measurement by mixing appropriate volumes of the stock solutions so that the concentration of 3,6-dinitronaphthalenedicarboxylic anhydride was kept constant at each temperature ($2{\cdot}20 \times 10^{-4}$M at 2·9°, $2{\cdot}5 \times 10^{-4}$M at 27·5°, and $3{\cdot}19 \times 10^{-4}$M at 41·0°) and the concentration of pyrene was varied over the range $0{\cdot}5 \times 10^{-1}$—$2{\cdot}7 \times 10^{-1}$M. A solution of 3,6-dinitronaphthalenedicarboxylic anhydride of the same concentration as in the solution under study was used as the reference. Each optical density measurement was repeated three times and the average value was taken.

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Introduction to Molecular Photochemistry

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LONDON
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Preface

The expansion of interest in photochemistry over the past decade is reflected by the large number of research papers and reviews of photochemical research which have been published during this period. The growth of photochemistry is connected to some extent to the realization by researchers that many of the concepts of molecular electronic spectroscopy are applicable to photochemistry, and a language linking photochemistry and electronic spectroscopy has now arisen. The research work over the past decade has laid the foundations for the understanding of photochemical and photophysical processes, and photochemistry is now being taught in most Universities, Polytechnics and Colleges as part of the undergraduate teaching programme. Although a number of texts on photochemistry have appeared in recent years these are mainly at final-year undergraduate and post-graduate level and it is felt that there is a need now for an introductory undergraduate text on the subject.

The object of the book is to present the principles of molecular photochemistry in a form suitable for undergraduate students new to photochemistry and to electronic spectroscopy. It is hoped that it may also be useful to post-graduate students and research workers seeking a concise introduction to photochemistry. The first chapter is concerned with the properties of electromagnetic radiation and the relationship between the absorption of radiation, absorption spectra and photochemistry. The second chapter develops the concepts of electronic transitions and absorption spectra, and this is followed in the third chapter by a discussion of electronically excited states and their properties. The fourth chapter deals with the kinetics of intramolecular and intermolecular processes, both chemical and physical, originating from excited state molecules. Some of the many photochemical

reactions undergone by organic compounds and those of a limited number of inorganic compounds are outlined in the fifth and sixth chapters. The fifth chapter is concerned mainly with different types of photochemical reaction, while the sixth chapter deals mainly with photofragmentation and related reactions in various classes of compound.

I would like to express my appreciation to my colleagues, Mr E. F. H. Brittain and Dr A. Vincent, for reading the manuscript and for making valuable comments and suggestions.

C. H. J. Wells

Kingston upon Thames
January, 1972

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有機光化学序論

C. H. J. WELLS 著
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FOREWORD TO THE JAPANESE EDITION

Photochemistry is now well established as an important branch of modern-day chemistry, and the realisation that radiation from the sun may be man's future energy source has given rise to an increase in the already considerable research activity in this area. The importance of photochemistry makes it desirable that the subject be taught in undergraduate chemistry courses, and it is hoped that the present volume will serve as a suitable undergraduate text for the teaching of photochemistry in Universities and Colleges in Japan.

C. H. J. WELLS

Kingston upon Thames
October, 1976

Studies on Nitroaromatic Compounds. Part V.[1] The Electron Spin Resonance Spectra of Some Symmetrically Substituted Polynitroacenaphthenes

By Brian C. Webb, Clifford H. J. Wells,* and James A. Wilson, School of Chemical Science and Technology, Kingston Polytechnic, Kingston upon Thames, Surrey

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Studies on Nitroaromatic Compounds. Part V.[1] The Electron Spin Resonance Spectra of Some Symmetrically Substituted Polynitroacenaphthenes

By Brian C. Webb, Clifford H. J. Wells,* and James A. Wilson, School of Chemical Science and Technology, Kingston Polytechnic, Kingston upon Thames, Surrey

The e.s.r. spectra of the radical anions of 3,8-dinitroacenaphthene and 3,5,6,8-tetranitroacenaphthene have been recorded at −40°. Proton and nitrogen hyperfine coupling constants have been assigned, where possible, on the basis of McLachlan MO calculations, and the spectra have been simulated using the values for the experimental coupling constants.

THERE are many examples where observed e.s.r. spectra of radical anions differ from theoretical spectra predicted on the basis of the usual isotropic hyperfine interaction between the unpaired electron and the magnetically active nuclei in the system. Modulation of the hyperfine coupling constants by migration of the counter ion between sites within the ion pair [2] or strong solvation of the radical anion [3,4] can lead to differences between the experimental and the predicted spectra, these differences being manifested by anomalous line broadening and line intensities in the experimental spectra. These anomalous effects have been observed in the e.s.r. spectra of the radical anions of a number of nitroaromatic

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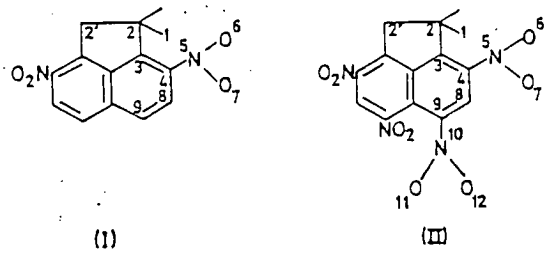
compounds.[2-14] The studies on nitroaromatic compounds have been restricted to nitrobenzenoid and nitronaphthalenic systems and in order to extend the range of investigations we have prepared the radical anions of 3,8-dinitroacenaphthene (I) and 3,5,6,8-tetranitroacenaphthene (II) and recorded their e.s.r. spectra.

RESULTS AND DISCUSSION

The numbering system used for the description of the radical anions (I) and (II) is given in the Scheme. The spin densities at the nuclear sites in the radical anions



(I) (II)

SCHEME

(Table 1) were calculated using the McLachlan approximate configuration interaction method,[15] the calculations being performed on the basis that hyperconjugation between the methylene protons and the electron system accounted for the electron–nuclear interaction at the methylene protons.[16-18] The values used in the calculations for the parameters h_x and k_{x-y} in the Coulombic integral $\alpha_x = \alpha + h_x\beta$ and the resonance integral $\beta_{xy} = k_{x-y}\beta$ respectively are given in Table 2. The theoretical proton coupling constants, a, listed in Table 1, were obtained from the calculated spin densities, ρ, using the McConnell equation (1) [19] where for the methylene protons and aromatic ring protons values of 254 [18]

$$a = Q\rho \qquad (1)$$

and 23·7 Oe [20] were chosen respectively for the Q term.

The theoretical nitrogen coupling constants, a_N, given in Table 1, were obtained from the calculated spin densities using equation (2) [21] where ρ_N and ρ_O are the

$$a_N = \pm 99\rho_N^{\pi} \mp 71{\cdot}6\,\rho_O^{\pi} \qquad (2)$$

spin densities at the nitrogen nucleus and at the neighbouring oxygen nucleus respectively.

The e.s.r. spectrum of radical anion (I) is shown in Figure 1(a) and that for radical anion (II) in Figure 2(a). The experimental coupling constants derived from these spectra are listed in Table 1. There is no apparent linewidth alternation in the spectra under the experimental conditions used and the spectra could be simulated satisfactorily using the experimental coupling constants and integer ratios for the predicted line intensities [Figures 1(b) and 2(b)].

The spectrum of radical anion (I) can be analysed in terms of electron–nuclear spin interaction involving four equivalent protons, two equivalent nitrogens, and two pairs of equivalent protons. The basic pattern in the spectrum is that of a triplet of triplets and this, taken in conjunction with the values for the calculated coupling constants, indicates that the major splittings arise from interaction with the two pairs of aromatic ring protons.

TABLE 1

Spin densities and coupling constants for polynitroacenaphthene radical anions

Radical anion	Position [a]	McLachlan spin densities	Proton coupling constants (Oe) Theor.[b]	Proton coupling constants (Oe) Expt.	Nitrogen coupling constants (Oe) Theor.[c]	Nitrogen coupling constants (Oe) Expt.
(I)	1(H)	0·0014	0·36	0·25		
	8(H)	0·0042	0·10	2·16, 2·81 [d]		
	9(H)	0·1212	2·87	2·16, 2·81 [d]		
	5(N)	0·0088			0·27	0·25
	6,7(O)	0·0160				
(II)	1(H)	0·0013	0·33	0·32		
	8(H)	0·0921	2·18	2·74		
	5(N)	0·0020			0·49	0·42, 0·44 [d]
	6,7(O)	−0·0041				
	10(N)	0·0075			0·36	0·42, 0·44 [d]
	11,12(O)	0·0154				

[a] Numbering system refers to the structures shown in the Scheme. [b] Calculated from equation (1). [c] Calculated from equation (2). [d] Cannot be unambiguously assigned.

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The experimental values for the coupling constants of these protons are similar (2·16 and 2·81 Oe) and it is not possible to use the calculated values to assign the couplings to specific protons. In view of the similarity between the experimental values it is surprising that there is such a large difference between the calculated values for positions 8(H) and 9(H) (Table 1). The presence of

TABLE 2

MO Parameters used in calculations

Position [a]	h_x	Bond [a]	k_{x-y}
1(H)	−0·40	1–2(C–H)	3·0
2(C)	−0·35	2–3(C–C)	0·2
3(C)	−0·0,[b] −0·35 [c]	2–2′(C–C)	0·8
		4–5(C–N)	1·8
5,10(N)	2·2	5–6,7(N–O)	2·4
6,7,11,12(O)	1·2	9–10(C–N)	1·2
		10–11,12(N–O)	2·4

[a] Numbering system refers to the structures shown in the Scheme. [b] Value used for radical anion (I). [c] Value used for radical anion (II).

the nitro-groups obviously has a marked effect since the experimental coupling constants for the positions corresponding to 8(H) and 9(H) in the radical anion of acenaphthene are notably different and there is good agreement between the experimental and theoretical values.[18] The molecular orbital parameters used for the nitro-group determine the agreement between the experimental and calculated coupling constants, and in the present work some sixty calculations were performed with gradual variation of the parameters until the best fit was obtained with those parameters quoted in Table 2. It did not prove possible to find a set of parameters which gave similar values for the coupling constants at positions 8(H) and 9(H) and at the same

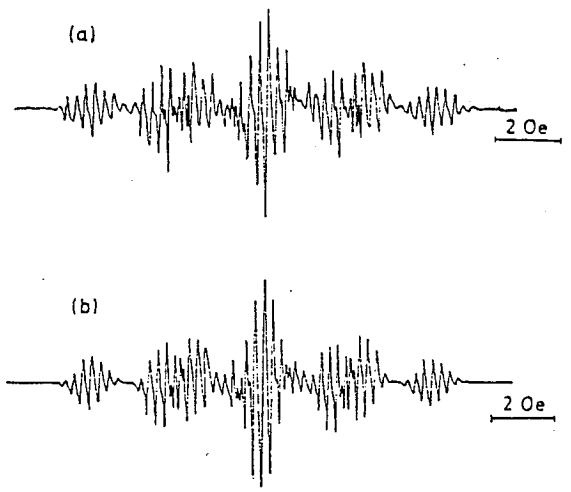

FIGURE 1 First derivative e.s.r. spectrum of the radical anion of 3,8-dinitroacenaphthene at −40 °C; (a) experimentally observed; (b) simulated

time gave reasonable agreement between the experimental and calculated coupling constants for the other magnetically active sites in radical anions (I) and (II).

The experimental coupling constants for interaction at the nitrogen nuclei and at the bridge protons in radical anion (I) have the same value and the agreement with the calculated values is reasonable. The coupling constant for the bridge protons in radical anion (I) is much

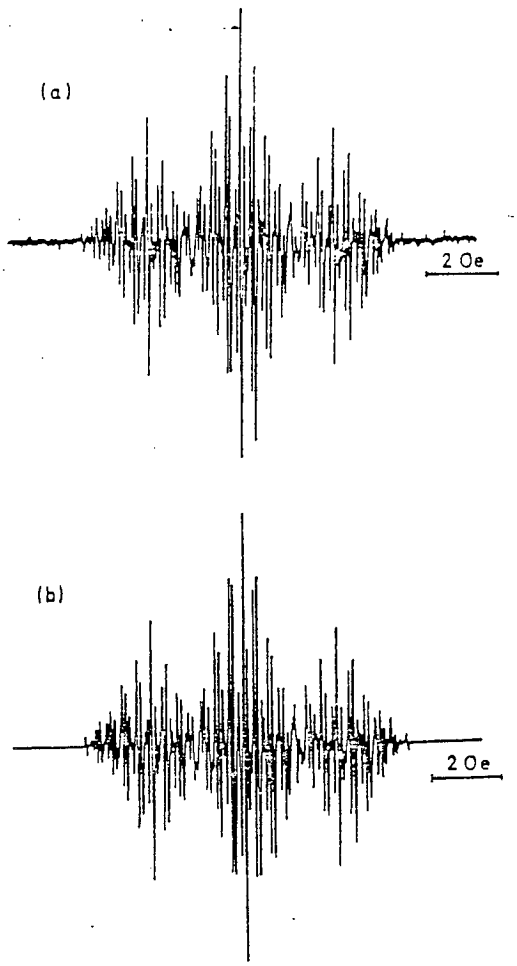

FIGURE 2 First derivative e.s.r. spectrum of the radical anion of 3,5,6,8-tetranitroacenaphthene at −40 °C: (a) experimentally observed; (b) simulated

lower than the corresponding value for the radical anion of acenaphthene (7·53 Oe),[18] presumably because of the electron-withdrawing properties of the *ortho*-substituted nitro-groups in radical anion (I).

The spectrum of radical anion (II) can be analysed in terms of splittings from two equivalent protons, two pairs of equivalent nitrogens, and four equivalent proton nuclei. There is good agreement between the values for the experimental and theoretical proton coupling constants and this allows the proton coupling constants to be assigned unambiguously to specific protons. Here, as for radical anion (I), the major splitting arises from interaction with the aromatic ring protons and the spectrum exhibits a basic triplet pattern. Although the values for the theoretical nitrogen coupling constants agree well with the experimental values the difference

between the experimental values is too small to allow an unambiguous assignment to be made.

EXPERIMENTAL

3,8-Dinitroacenaphthene was prepared by a reported method.[22] 3,5,6,8-Tetranitroacenaphthene was prepared by the method of Vernon and Wilson [23] with the modification that recrystallisation was performed using nitromethane instead of benzene. 5,6-Dinitroacenaphthene was prepared by a literature method.[24] The synthesis of the unreported compound 4,7-dinitroacenaphthene was attempted but was not successful

The radical anions of 3,8-dinitroacenaphthene and 3,5,6,8-tetranitroacenaphthene were prepared by reduction with sodium.[25] Repeated attempts to prepare the radical anion of 5,6-dinitroacenaphthene by the same method were unsuccessful. The 1,2-dimethoxyethane which was used as solvent was dried over sodium, trap-to-trap distilled from alumina and sodium hydroxide pellets onto sodium and anthracene, and stored under vacuum.

The e.s.r. spectra of the radical anions were recorded at −40° on a Varian E-4 spectrometer. The experimental proton and nitrogen coupling constants derived from the spectra were checked by simulating the spectra using a computer program based on a Lorentzian line-shape function.

We thank Dr. J. A. Paxton, Varian Associates Ltd., and Dr. A. Hudson, University of Sussex, for providing instrumental facilities for this work.

[2/2284 *Received, 4th October,* 1972]

[22] B. C. Webb and C. H. J. Wells, *J.C.S. Perkin I*, 1972, 166.
[23] F. Vernon and R. D. Wilson, *Tetrahedron*, 1965, **21**, 2719.
[24] M. M. Dashevskii and Z. P. Malevannaya, *J. Gen. Chem. U.S.S.R.*, 1964, **34**, 521.
[25] C. H. J. Wells and J. A. Wilson, *J. Chem. Soc.* (*B*), 1971, 1588.

The Positive and Negative Ion Mass Spectra of Some Nitro- and Polynitro-acenaphthenes

By **John F. J. Todd** * and **Robert B. Turner**, University Chemical Laboratory, University of Kent at Canterbury
Brian C. Webb and **Clifford H. J. Wells**,* School of Chemical Science and Technology, Kingston Polytechnic Kingston-upon-Thames, Surrey

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The Positive and Negative Ion Mass Spectra of Some Nitro- and Polynitro-acenaphthenes

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The positive and negative ion 70 eV mass spectra of thirteen nitro- and polynitro-acenaphthenes are reported. The postulated fragmentation patns, many of which are supported by metastable ion evidence, are interpreted in terms of structural features of the molecules and stabilities of the products formed. The significant similarities and differences between the two types of spectra are rationalised where possible.

THE positive ion mass spectra of simple nitroaromatics are now relatively well characterised,[1] the compounds studied including nitrobenzene, the mononitrotoluenes, nitroanilines, and nitrophenols.[2] Numerous mono- and di-nitronaphthalenes have also been investigated.[3,4] The negative ion mass spectra of these compounds have received considerably less attention, the only significant publications having appeared within the last two years. Brown and Weber[5] have reported upon the negative ion spectra of *m*- and *p*-dinitrobenzenes obtained with 2—20 eV electrons, and Bowie and his co-workers have discussed the negative ion mass spectra of the isomeric nitrophthalic anhydrides[6] and *N*-substituted nitroanilines,[7] as well as a series of nitrobenzenes containing substituent groups such as formyl and carboxy[8] and trifluoroacetamido.[9] Direct comparisons between positive and negative ion mass spectra within the same publication are extremely rare, although one recent example is the report by Larkins *et al.*[10] on a series of substituted trinitromethanes.

In this account we discuss the positive and negative ion mass spectra of a series of nitro- and polynitro-acenaphthenes, a group of compounds not previously subjected to mass spectral analysis, and consider the extent to which the two types of spectra relate both to each other and to the published data on other nitro-compounds.

DISCUSSION

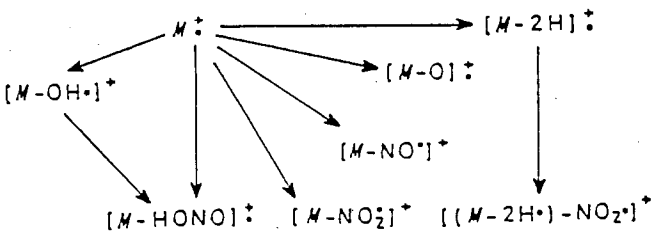
(*A*) *The Positive Ion Mass Spectra.*—The most abundant ions in the spectra of the nitroacenaphthenes are listed in Table 1 along with the value for the percentage total ion current carried by each ion. These values when taken in conjunction with the metastable ion evidence for specific decay processes suggest that the molecular ions fragment in the main by the routes shown in Scheme 1. The molecular ions are relatively stable and although

TABLE 1

Metastable transitions [a] and percentage total ion current for important fragmentations in the positive ion spectra of nitroacenaphthenes

		Daughter ions															
		[(*M* − OH·) − NO·]⁺⁺															
		[*M* − OH·]⁺		(or [*M* − HONO]⁺)		[*M* − NO·]⁺		[*M* − NO_2·]⁺		[(*M* − NO_2·) − NO·]⁺⁺		[*M* − O]⁺⁺		[*M* − H_2]⁺⁺		[(*M* − H_2) − NO_2·]⁺	
Substitution pattern	*M*⁺⁺ (%)	*m**	%	*m** [b]	%	*m**	%	*m**	%	*m**	%	*m**	%		%		%
3-(I)	14·4	*	16·6	(*)	22·5		0·8	*	5·7		0·0		2·4		1·1		6·4
4-(II)	23·9		1·5	*	16·6	*	0·9	*	17·6		0·1		0·3		0·0		5·9
5-(III)	19·6	*	3·7	*	16·4	*	2·3	*	9·1		0·1		0·8		0·1		4·6
3,6-(IV)	13·8		16·4	(*)	3·7	*	0·2		1·4		1·4		2·6		0·1		0·7
3,7-(V)	12·1	*	15·2	*	5·6		0·0		1·8	*	0·0		2·4		0·0		0·8
3,8-(VI)	17·1	*	18·5		1·9		0·2		1·1	*	1·0		2·8		0·2		0·7
4,5-(VII)	17·6		0·2		0·0	*	0·1		2·0		0·2		0·0		0·0		0·1
4,6-(VIII)	32·5	*	3·1	(*)	1·0	*	1·5	*	3·8	*	2·0		0·7		0·1		0·2
5,6-(IX)	14·7	*	0·1	(*)	0·1	*	0·1	*	6·8	*	18·3		0·3		0·1		0·1
3,5,6-(X)	5·8	*	1·8		0·6		0·0	*	2·8		2·3		0·4		0·4		0·8
3,5,8-(XI)	12·2	*	12·0	(*)	3·1	*	0·1		0·7	*	0·3		1·9		3·6		1·2
3,5,6,7-(XII)	5·2	*	3·2	*	0·2		0·3		1·1	*	0·5		0·7		2·7		2·9
3,5,6,8-(XIII)	4·4	*	1·6	(*)	0·5		0·9	*	0·6		0·1		0·4		3·4		6·3

[a] Asterisk in Table indicates that metastable ion observed at appropriate *m/e* value. [b] Parentheses indicate metastable ions observed for the transitions [*M* − OH·] − NO·]⁺⁺ and [*M* − HONO]⁺⁺. The remaining metastable ions are for the transition [(*M* − OH·) − NO·]⁺⁺ only.



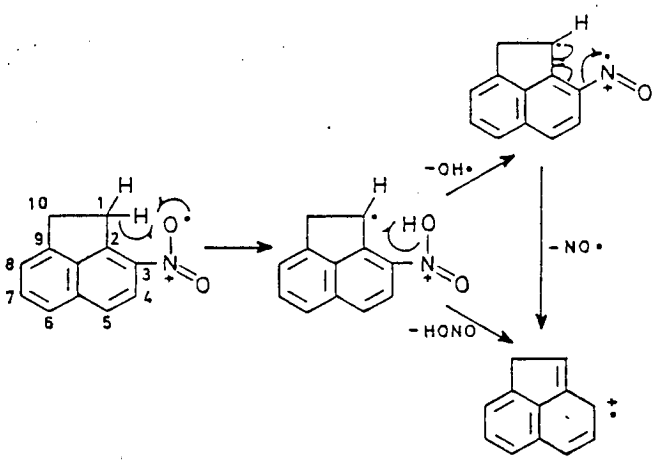
SCHEME 1

In this account we discuss the positive and negative ion mass spectra of a series of nitro- and polynitro-acenaphthenes, a group of compounds not previously subjected to mass spectral analysis, and consider the

[1] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 517.
[2] J. H. Beynon, R. A. Saunders, and A. E. Williams, 'The Mass Spectra of Organic Molecules,' Elsevier, Amsterdam, 1968, pp. 322—334, 340—342.
[3] Ref. 2, pp. 334—339.
[4] E. F. H. Brittain, C. H. J. Wells, H. M. Paisley, and D. J. Stickley, *J. Chem. Soc.* (*B*), 1970, 1714.
[5] C. L. Brown and W. P. Weber, *J. Amer. Chem. Soc.*, 1970, 92, 5775.
[6] T. Blumenthal and J. H. Bowie, *Austral. J. Chem.*, 1971, 24, 1853.
[7] J. H. Bowie, T. Blumenthal, and I. Walsh, *Org. Mass Spectrometry*, 1971, 5, 777.
[8] J. H. Bowie, *Org. Mass Spectrometry*, 1971, 5, 945.
[9] J. H. Bowie, *Austral. J. Chem.*, 1971, 24, 989.
[10] J. T. Larkins, J. M. Nicholson, and F. E. Saalfeld, *Org. Mass Spectrometry*, 1971, 5, 265.

the stability is less for the tri- and tetra-nitroacenaphthenes than for the mono- and di-nitroacenaphthenes the molecular ion peak is still of significant intensity in the spectra of the former compounds.

Loss of hydroxyl radical and nitrous acid. The results show that the losses of OH· and HONO represent major fragmentation routes in the decomposition of the majority of compounds studied. Possible mechanisms for the expulsion of OH· and HONO from nitroacenaphthenes in which there is a nitro-group *ortho* to the aliphatic bridge system are shown for 3-nitroacenaphthene (I) in Scheme 2.



SCHEME 2

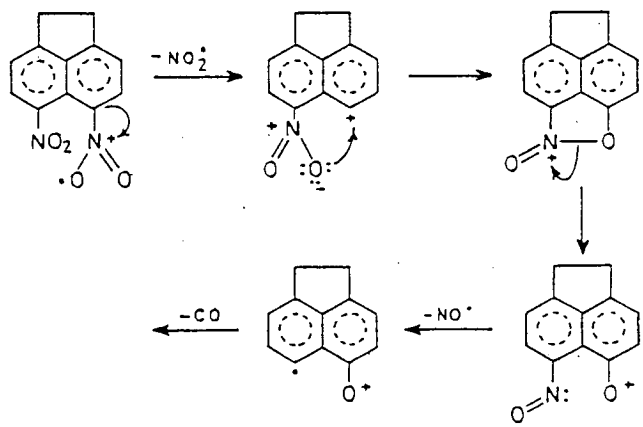
The loss of OH· *via* interaction of a nitro-group with a neighbouring alkyl group as shown in Scheme 2 is analogous to the fragmentation of the molecular ion of *o*-nitrotoluene.[11] However, whereas the $[M - OH\cdot]^+$ ion formed from *o*-nitrotoluene fragments further by sequential loss of CO and HCN, where the carbon atom lost as CO is the methyl carbon atom, this route for further fragmentation is not available to the $[M - OH\cdot]^+$ ions from nitroacenaphthenes since the elimination of CO by an analogous mechanism to that operative for *o*-nitrotoluene would involve rupture of two bonds in the aliphatic bridge. As expected, therefore, the peaks at *m/e* values corresponding to the $[(M - OH\cdot) - CO]^+$ ions and the $[(M - OH\cdot) - CO - HCN]^+$ ions are insignificant in the spectra of the nitroacenaphthenes.

Elimination of OH· and of HONO also occurs from those nitroacenaphthenes which are not substituted at the sites *ortho* to the aliphatic bridge. For such compounds the hydrogen abstraction step analogous to that shown in Scheme 2 will involve the neighbouring ring hydrogen atoms rather than the bridge hydrogen atoms. Previous reports on the loss of OH· from alkyl substituted nitroaromatics [11-14] suggest that in the case of 5-substituted derivatives the hydrogen would be preferentially abstracted from the ring not containing the nitro-group.

Loss of nitrogen dioxide and nitric oxide. The elimination of NO_2· from the molecular ion of the nitroacenaphthenes can occur by simple bond fission and in the majority of cases the corresponding metastable ion peak is observed in the spectra (Table 1). Similarly, the elimination of NO· from the molecular ions, presumably *via* the nitro ⟶ nitrito rearrangement,[15] is indicated in most cases by the presence of a metastable ion peak. These fragmentation processes do not warrant further comment except that insofar as their relative importance depends upon the structure of the nitroacenaphthene and the facility of the other competing primary fragmentation processes. The sequential loss of NO_2· and NO· is of greater interest since this process appears to be markedly structure-dependent as shown by the fact that the percentage total ion current for the $[(M - NO_2\cdot) - NO\cdot]^{+\cdot}$ ion is relatively low for all the compounds except 5,6-dinitroacenaphthene (IX) where the value is very high, *viz.* 18·3%. This last phenomenon can be rationalised in terms of the mechanism for sequential loss of NO_2· and NO· shown in Scheme 3.

One feature of Scheme 3 is that transfer of an oxygen atom from a nitro-group at the 5-position to C-6 can occur under favourable circumstances, *e.g.* a positive charge residing at C-6. The observation of a metastable ion peak in the spectrum of 5,6-dinitroacenaphthene corresponding to the loss of CO from the $[(M - NO_2\cdot) - NO\cdot]^{+\cdot}$ ion provides support for this oxygen transfer step.

Elimination of NO_2· followed by NO· does not play a prominent role in the fragmentation of the molecular ions of tri- and tetra-nitroacenaphthenes substituted at



SCHEME 3

the 5- and 6-positions since in these compounds alternative fragmentations, such as elimination of OH·, dominate the breakdown pattern.

Loss of hydrogen. A notable feature of the spectra of the nitroacenaphthenes is the increase in intensity of the $[M - H_2]^{+\cdot}$ peak as the number of nitro-groups in the compounds increases (Table 1). The loss of hydrogen is

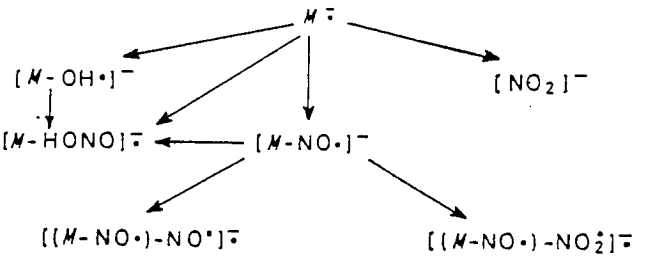
[11] S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, 1966, 88, 4974.
[12] J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc.* (*B*), 1966, 396.
[13] J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Naturforsch.*, 1966, 21a, 210.
[14] G. E. Robinson, C. B. Thomas, and J. M. Vernon, *J. Chem. Soc.* (*B*), 1971, 1273.
[15] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. belge*, 1964, 311.

likely to occur from the aliphatic bridge and the results in Table 1 suggest that the probability of loss increases as the Lewis acidity of the naphthalene system increases and the charge density on the aliphatic bridge decreases. This is supported by the results for the percentage total ion current for the $[M - H_2]^{+\cdot}$ ion from 3,5,6-trinitroacenaphthene (X) (0·4%) and 3,5,8-trinitroacenaphthene (XI) (3·6%). The Lewis acidity of the naphthalene system of (X) will be less than that of (XI) since in the former compound steric interaction between the nitro-groups at the 5- and 6-positions forces the groups out of the plane of the aromatic system and reduces their electron-withdrawing power. Thus the electron density in the aliphatic bridge of (XI) will be lower than that in (X). Also, the inductive effect of the two *ortho*-nitro-groups in (XI) as compared to that of the one *ortho*-nitro-group in (X) will be such that the electron density will be lower in the aliphatic bridge of the former compound. Similarly, the electron density in the aliphatic bridge of 3,5,6,8-tetranitroacenaphthene (XIII) will be less than that in 3,5,6,7-tetranitroacenaphthene (XII) and here the percentage total ion currents carried by the $[M - H_2]^{+\cdot}$ ions are 3·4 and 2·7 respectively. The small values for the percentage total ion current for the $[M - H_2]^{+\cdot}$ ion in the spectra of the mononitro- and dinitro-derivatives suggest that the electron density in the aliphatic bridge in these compounds is not sufficiently low for the elimination of H_2 to be an energetically favoured process compared with the other primary fragmentation routes.

Loss of atomic oxygen. The values given in Table 1 for the percentage total ion current for the $[M - O]^{+\cdot}$ ion show that the elimination of an oxygen atom is favoured when there is a nitro-group *ortho* to the aliphatic bridge. A similar, though less marked, effect is observed in the spectra of mononitrotoluenes.[11] The mechanism whereby the neighbouring alkyl group in the *ortho*-substituted nitroacenaphthenes and in *o*-nitrotoluene enhances the loss of an oxygen atom is open to conjecture.

Loss of carbon monoxide. It is of interest that nitroacenaphthenes substituted at the 5-position but not at the 6-position do *not* undergo significant loss of CO from the molecular ion whereas for nitronaphthalenes substituted at the 1-position but not at the 8-position the loss of CO from the molecular ion is a major fragmentation process.[4,13] The elimination of CO from nitronaphthalenes of this type is dependent upon the transfer of an oxygen atom from the nitro-group to C-8. The difference between the nitroacenaphthenes and the nitronaphthalenes could arise because the C-5–C-5a–C-6 bond angle in the acenaphthene skeleton is greater than the corresponding bond angle in the naphthalene skeleton,[16] a factor which has been invoked[17] to explain the observation that the rate of nitration at the 5-position of acenaphthene is seventeen times greater than that at the 4-position in 1,8-dimethylnaphthalene. The increased bond angle results in an increased separation between the oxygen and the adjacent *peri*-carbon atom in nitroacenaphthenes relative to that in nitronaphthalenes with the effect that oxygen transfer is likely to be inhibited. Nevertheless under favourable conditions (see above) the oxygen transfer step can compete effectively with other processes involved in the fragmentation of the positive ions.

(*B*) *The Negative Ion Mass Spectra.—General features.* The percentage total ion current carried by each of the major negative ions produced from the nitroacenaphthenes is given in Table 2, as are the observed metastable ion transitions. As can be seen the majority of the molecular anions formed are highly stable and for nine of the compounds studied the molecular ion peaks are also the base peaks of the spectra. The most prominent routes for fragmentation of the molecular ions involve loss of hydroxyl radical, nitrous acid, nitric oxide, and nitrite. These primary fragmentations and the major subsequent fragmentations are summarised in Scheme 4.



SCHEME 4

Loss of hydroxyl radical and nitrous acid. As can be seen from Table 2 the loss of hydroxyl radical and of nitrous acid from 4,5-dinitroacenaphthene, 4,6-dinitroacenaphthene, and 5,6-dinitroacenaphthene is significantly less than the corresponding losses from the remainder of the polynitroacenaphthenes which all have a nitro-group positioned *ortho* to the aliphatic bridge. This indicates that the losses involve abstraction of a hydrogen atom from the aliphatic bridge system by the nitro-group. The presence of a further nitro-group in an analogous *meta*-position to the *ortho*-substituted group facilitates the losses by resonance delocalisation of the negative charge that remains after the hydroxyl radical or nitrous acid is removed. This is exemplified for 3,8-dinitroacenaphthene in Scheme 5. It is significant that the combined yield of $[M - OH\cdot]^-$ and $[M - HONO]^{-\cdot}$ ions from 3,8-dinitroacenaphthene, in which there are two nitro-groups *ortho* to the aliphatic bridge is much greater than that from 3,6-dinitroacenaphthene in which the nitro-groups are in analogous *meta*-positions but only one group is *ortho* to the aliphatic bridge. In the case of 3,5,8-trinitro- and 3,5,6,8-tetranitro-acenaphthene there are two and three nitro-groups respectively which are in analogous *meta*-positions to the nitro-groups *ortho* to the aliphatic bridge. Also, since there are two nitro-groups *ortho* to the bridge in both compounds, the likelihood of loss of OH· would be expected to be high. In fact the peak corresponding to the

[16] H. W. W. Ehrlich, *Acta Cryst.*, 1957, **10**, 699.
[17] A. Davies and K. D. Warren, *J. Chem. Soc.* (*B*), 1969, 873.

$[M - OH\cdot]^-$ ion is the base peak in the spectrum of each of these compounds.

Loss of nitric oxide. It has been suggested by Bowie *et al.*[7] that the loss of NO· from nitroaromatic compounds is facilitated when an *ortho/para* electron-withdrawing group is present. This is thought to arise because of resonance stabilisation of the phenoxide ion which results from loss of NO·. It is thus to be expected that the loss of NO· will be favoured in compounds containing a nitro-group in an effective *ortho/para* position relative to the nitro-group from which the loss eventually occurs. Presumably this fragmentation is preceded by a nitro ⟶ nitrito rearrangement as is shown for 4,6-dinitro-acenaphthene in Scheme 6. 3,7-Dinitro-, 4,5-dinitro-, and 4,6-dinitro-acenaphthene all have nitro-groups which are effectively *ortho/para* to each other and it can be seen from Table 2 that the relative abundance of the $[M - NO\cdot]$ ion from these compounds is far higher than for any of the other compounds studied. 3,5,6,7-Tetra-nitroacenaphthene is the only other compound in which nitro-groups are effectively *ortho/para* substituted but here nitro-groups are also in *meta*-positions to each other. The mixed *ortho/para*- and *meta*-character of this compound is reflected in its negative ion spectrum in that the yield of the $[M - NO\cdot]^-$ ion is similar to the combined yield of the $[M - OH\cdot]^-$ and $[M - HONO]^-$ ions.

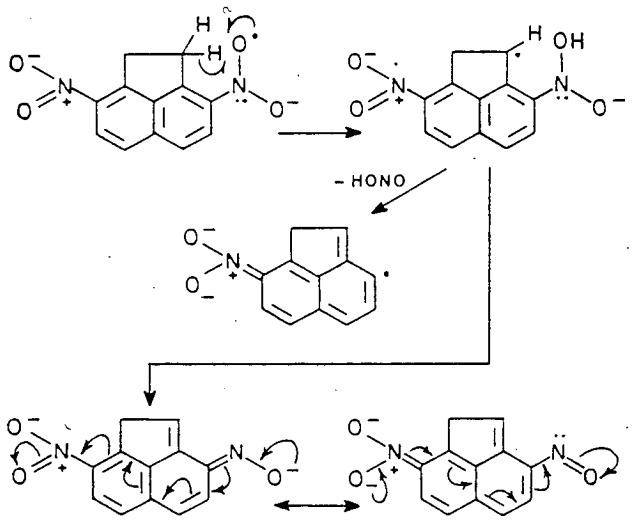
Formation of nitrite ion. Loss of the nitrite ion from the molecular anions is a particularly prominent feature of the negative ion spectra. However the percentage total ion carried by this ion is less easy to correlate directly with the structure of the parent ion than is the case for the other major ions. No metastable ion was observed for the formation of the nitrite ion and it may be concluded that it must be produced by a rapid process, *e.g.* dissociative electron capture.

TABLE 2

Metastable transitions [a] and percentage total ion current for important fragmentations in the negative ion mass spectra of nitroacenaphthenes

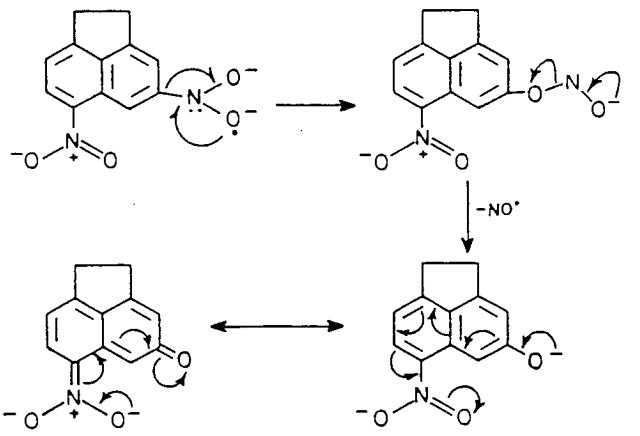
		Daughter ions																	
		$[M - OH\cdot]^-$		$[(M - OH\cdot) - NO\cdot]^{-\cdot}$ (or $[M - HONO]^{-\cdot}$)		$[M - NO\cdot]^-$		$[(M - NO\cdot) - NO\cdot]^{-\cdot}$		$[M - NO_2\cdot]^-$		$[(M - NO\cdot) - NO_2\cdot]^{-\cdot}$		$[M - O]^{-\cdot}$	$[M - H\cdot]^-$	$[M - H_2]^{-\cdot}$	$[(M - H_2) - NO\cdot]^-$	NO_2^-
Substitution pattern	$M^{-\cdot}$ (%)	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%	%	%	%	%	%
3-(I)	64·6		0·6				1·6							0·5	1·3			16·7
4-(II)	63·3		0·0				0·1							0·3	1·1	5·5	0·4	18·3
5-(III)	27·4		0·7		0·2		3·0				0·3			1·1	1·5	0·3	0·3	49·0
3,6-(IV)	21·2	*	3·2		1·7	*	5·3	*	1·4		0·6		0·6	0·6	3·7	0·2	0·7	42·3
3,7-(V)	9·4		1·9	*[b]	5·6	*	18·9	*	3·6		1·4		0·7	0·8	1·3	0·1	0·4	41·7
3,8(VI)	28·0	*	6·5		2·0	*	3·2	*	0·8		0·7		0·7	0·8	0·9	0·2	0·5	33·5
4,5-(VII)	15·2		0·0		0·0	*	16·1		0·0		1·5		0·0	0·0	0·0	0·0	0·0	65·5
4,6-(VIII)	32·6		0·0		0·6	*	15·1	*	1·2		0·5	*	0·3	1·4	0·3	0·3	0·9	38·4
5,6-(IX)	26·2		0·0		0·8	*	0·7	*	0·1		0·3		1·4	0·0	0·9	0·0	0·1	61·1
3,5,6-(X)	16·8	*	8·7		1·2	*	4·0	*	0·6		1·0	*	3·4	0·0	5·4	0·9	0·7	18·1
3,5,8-(XI)	7·9	*	19·3	*[c]	3·6	*	3·6	*	1·0		1·8	*	1·8	3·0	1·8	0·7	1·3	9·1
3,5,6,7-(XII)	13·0	*	5·2		2·2	*	6·3		0·5	*	8·6	*	3·7	0·8	0·5	1·6	1·9	3·2
3,5,6,8-(XIII)	4·7	*	18·8		3·0	*	1·7		0·5	*	1·8	*[d]	6·7	3·4	1·3	3·4	4·0	2·1

[a] Asterisk in Table indicates that metastable ion observed at appropriate m/e value. [b] Corresponding to $[(M - NO\cdot) - OH\cdot]^{-\cdot}$. [c] Corresponding to $[(M - OH\cdot) - NO\cdot]^{-\cdot}$. [d] Metastable ions indicate $[(M - NO_2\cdot) - NO\cdot]^{-\cdot}$ also formed.



SCHEME 5

(C) *Comparison of Spectra.*—In their study of the negative and positive ion mass spectra of trinitro-methanes, Larkins *et al.*[10] considered that there was little correlation between the peak intensities in the two types of spectra. In the present work, ionisation with 70 eV electrons should place negative ion formation in the domain of ion-pair formation [18] with zero yield of parent



SCHEME 6

[18] C. E. Melton in 'Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York and London, 1963, ch. 4.

ions.[19] That this latter effect is clearly not observed in these spectra is consistent with the suggestion made recently by McAllister [20] that at 70 eV there is a sufficiently high density of slow-moving secondary electrons (accompanying positive ion formation or emitted from electrode surfaces) to make electron attachment and dissociative attachment significant processes under these conditions. On this basis the axiomatic approach to the fragmentation of the primary molecular anions, suggested recently by Alexander *et al.*[21] should be applicable to these compounds.

If ion-pair formation is of importance one might expect to see similar trends in the yields of complementary pairs of ions between the two sets of spectra. Such a pair might be $[M - NO_2\cdot]^+$ and NO_2^-. In fact there is no apparent correlation of intensities over the range of compounds studied, and furthermore other ions which could be considered to be a complementary pair were not observed to be of importance in the spectra. The metastable ion evidence in the negative ion spectra clearly points to the fragmentation of the molecular anion, principally by expulsion of neutral species such as OH·, HONO, NO·, and to a lesser extent $NO_2\cdot$. These modes of fragmentation show fairly clear parallels in the behaviour observed for both sets of ions, *e.g.* there is the requirement in both series of spectra that a nitro-group be situated *ortho* to the aliphatic bridge for loss of hydroxyl radical from the molecular ion to be generally easy. On the other hand the balance between the tendency to lose NO· or $NO_2\cdot$ is quite different: whereas the former is principally expelled in negative ion fragmentations, with the latter being of only minor importance, the reverse situation is observed in the positive ion mass spectra. This might suggest that the anionic parent species is the more stable insofar as the loss of NO· must in general be preceeded by the nitro ⟶ nitrito rearrangement.

There is some similarity in behaviour between the two sets of spectra in the trends of the yields of ions formed by expulsion of H_2 from the molecular ion, where it appears that in both cases an increase in the number of electron-withdrawing substituents renders the bridge hydrogens more labile. Similar trends are also observed in the ions formed by sequential losses: $[(M - H_2) - NO\cdot]^-$ and $[(M - H_2) - NO_2\cdot]^+$.

EXPERIMENTAL

The synthesis of the compounds studied has been described elsewhere.[22] All the compounds were isomerically pure, with the exception of 5-nitroacenaphthene from which it did not prove possible to separate traces of the 3-nitro-compound.[23] The mass spectra were recorded on AEI MS9 and MS902 instruments operating at source pressures of *ca.* 10^{-6} Torr and temperatures of 150—220 °C. Assignment of the negative ion peaks was assisted by the use of an AEI 'Massmaster' modified for use with negative ion mass spectra.[24]

We thank the S.R.C. for a research grant in partial support of this work and Mr. R. G. Alexander for helpful discussions.

[2/2109 *Received*, 7*th September*, 1972]

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THE SYNTHESIS OF SOME NEW POLYNITRO-2,3-DIMETHYLNAPHTHALENES

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Abstract—The polynitration of derivatives of 2,3-dimethylnaphthalene has been investigated.

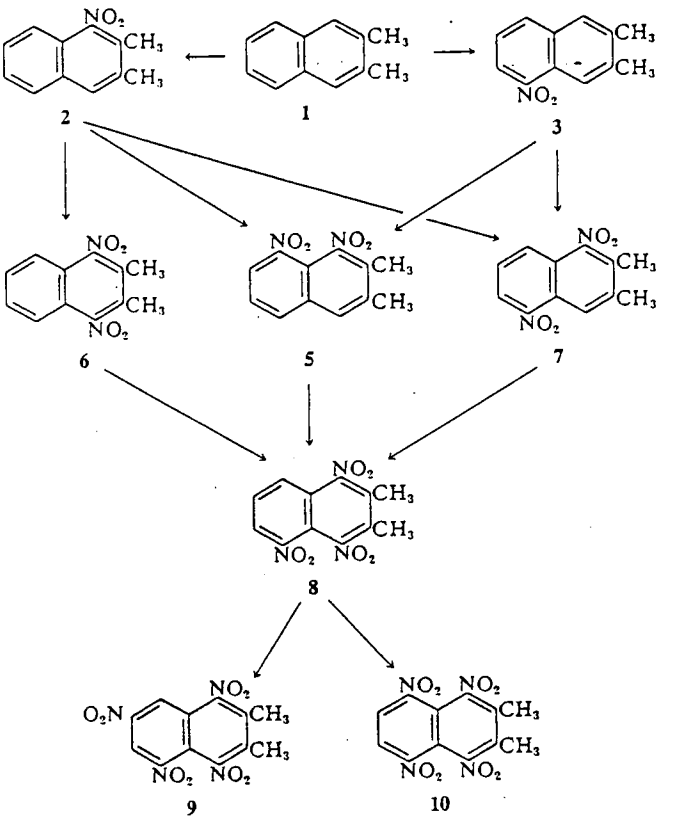
The nitration of methylbenzenes has been extensively studied, but relatively few investigations have been concerned with the nitration of methylnaphthalenes.

The mononitration of 1- and 2-methylnaphthalene has been reported in some detail,[1,2] as has the mononitration of a number of the isomeric dimethylnaphthalenes.[3] The synthesis of polynitrodimethylnaphthalenes has been limited to the preparation of dinitro derivatives,[4–7] except in the case of 2,6-dimethylnaphthalene from which a tetranitro derivative has been prepared.[7] The lack of information on synthetic routes to polynitrodimethylnaphthalenes is surprising since such compounds might be expected to exhibit explosive properties similar to the structurally similar polynitrotoluenes, and might be expected to be intermediates in the preparation of thermally stable explosives[8] having applications in space research.[9,10] In view of this, we have studied the nitration of methylnaphthalenes and dimethylnaphthalenes, and we now report on the synthesis of some new polynitro-2,3-dimethylnaphthalenes. Prior to this work, the only reported derivatives of 2,3-dimethylnaphthalene (1) were 1-nitro-2,3-dimethylnaphthalene (2),[3] 5-nitro-2,3-dimethylnaphthalene (3),[3] 6-nitro-2,3-dimethylnaphthalene (4)[3] and 1,8-dinitro-2,3-dimethylnaphthalene (5).[5]

Nitration of 1 with nitric acid in acetic anhydride gave a product mixture from which 1,4-dinitro-2,3-dimethylnapthalene (6), 1,5-dinitro-2,3-dimethylnaphthalene (7) and 5 were separated by fractional crystallisation and column chromatography. Undoubtedly the dinitro-compounds are formed via the intermediacy of 2 and 3 as shown in Scheme 1. In accord with this, the nitration of 2 in acetic anhydride yielded a mixture of 5, 6 and 7. The ratio of the isomers in the latter product mixture, as determined by NMR spectroscopy, was *ca* 1:1:1. It may be inferred from this ratio that the deactivating effect of the nitro group in the methyl substituted ring counterbalances to some extent the activating influence of the methyl groups, with the overall result that the rate of nitration in the methylated ring is similar to that for the non-methylated ring. Obviously, the presence of a nitro group in the non-methylated ring as in 3 would deactivate this ring towards nitration relative to the methylated ring and, as was to be expected, nitration of 3 with nitric acid/acetic anhydride gave a product mixture comprised solely of 5 and 7. The NMR spectrum of the product mixture showed that the isomer ratio was *ca* 60:40, indicating that nitration occurred at the 4-position in 3 in preference to the 1-position. This presumably arises because the 4-position is "*meta*" to the nitro group in 3 and as such is a favoured site for nitration. Obviously electronic effects have a greater influence than steric effects in determining the preferred site of nitration since the 1-position in 3 is less sterically hindered than the 4-position.

Conversion of 5, 6 and 7 into 1,4,5-trinitro-2,3-dimethylnaphthalene (8) can be achieved by nitration with the stoichiometric amount of nitric acid dissolved in sulphuric acid. As far as could be determined by NMR spectroscopy, 8 is the sole product in each of the reactions. Nitration of 8 in a mixture of nitric acid and sulphuric acid gives 1,4,5,7-tetranitro-2,3-dimethylnaphthalene (9) and a small yield of 1,4,5,8-tetranitro-2,3-dimethylnaphthalene (10). 9 can be isolated by fractional crystallization but it was not possible to isolate 10. However, this latter compound can be synthesised by an indirect route (see below). The various steps in the conversion of 2,3-dimethylnaphthalene into the tetranitrocompounds 9 and 10 are summarised in Scheme 1.

The synthesis of polynitro-2,3-dimethylnaphthalenes having nitro substituents in the non-methylated ring only, or having a greater number of nitro groups in the non-methylated ring than in the methylated ring can be achieved via the intermediacy of 5-amino or 5-acetamido derivatives of 2,3-dimethylnaphthalene. For instance, 5-amino-8-nitro-2,3-dimethylnaphthalene (11) is obtained on treatment of 3 with alkaline hydroxylamine, and can be diazotised and treated with sodium

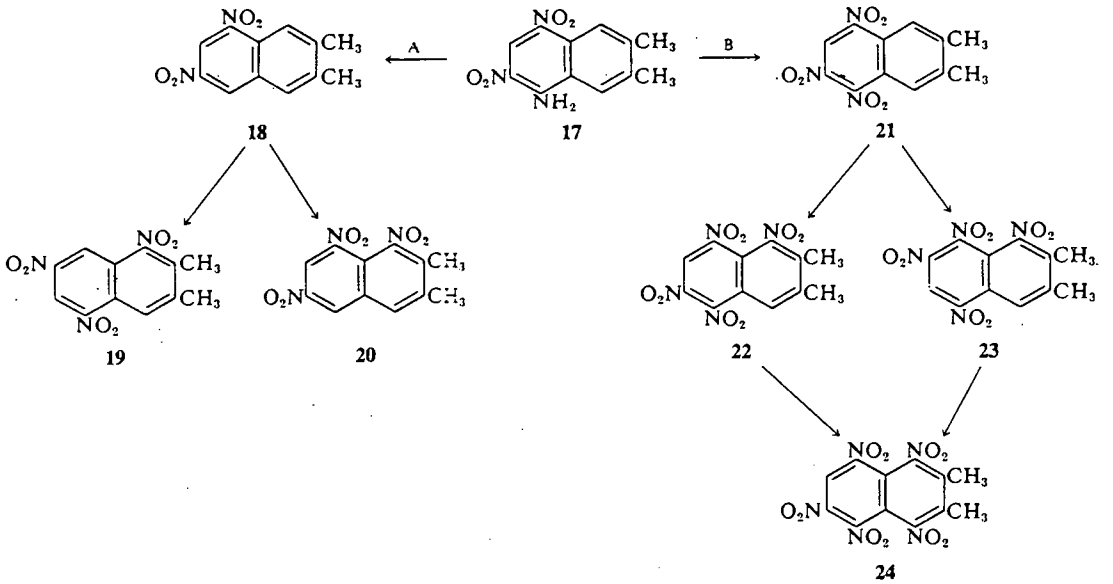


SCHEME 1

nitrite to yield 5,8-dinitro-2,3-dimethylnaphthalene (12). Nitration of this latter compound using the required amount of nitric acid for mononitration results in substitution in the methylated ring to give 1,5,8-trinitro-2,3-dimethylnaphthalene (13) as the only product. Nitration of 13 with excess of mixed acid takes the reaction through to the tetranitro stage, and here 1,4,5,8-tetranitro-2,3-dimethylnaphthalene (10) is the only product.

Reaction of 5-amino-2,3-dimethylnaphthalene (14) with a 1:1 mixture of acetic anhydride/acetic acid yields 5-acetamido-2,3-dimethylnaphthalene (15). The acetamido group in this latter compound activates the nonmethylated ring such that nitration using nitric acid/acetic anhydride results in substitution in the non-methylated ring only. Thus, dinitration of 15 gives 5-acetamido-6,8-dinitro-2,3-dimethylnaphthalene (16) as the only detectable product. Hydrolysis of 16 results in the formation of 5-amino-6,8-dinitro-2,3-dimethylnaphthalene (17), an intermediate which can be used to prepare tri-, tetra- and pentanitro-derivatives of 2,3-dimethylnaphthalene in which the number of nitro groups in the nonmethylated ring exceeds that in the methylated ring (see Scheme 2).

Route A in Scheme 2 is initiated by removing the amino group from 17 via diazotisation to yield 5,7-dinitro-2,3-dimethylnaphthalene (18). Nitration of the latter compound in mixed nitric/sulphuric acid using the stoichiometric amount of nitric acid for conversion to trinitro products gave a 30:70 mixture of 1,5,7-trinitro-2,3-dimethylnaphthalene (19) and 1,6,8-trinitro-2,3-dimethylnaphthalene (20). 19 and 20 were separated by column chromatography, and their structures assigned from their NMR and mass spectra. The compounds are not distinguishable from each other by their NMR spectra but are distinguishable by their mass spectra. Thus, the $(M-NO_2)^+$ ion gives rise to the base peak in the spectrum of 20, a feature characteristic of polynitronaphthalenes having nitro groups in adjacent *peri*-positions,[11] whereas the M^+ ion gives rise to the base peak in the spectrum of 19, a feature characteristic of polynitronaphthalenes having only one of the *peri*-positions occupied.[11] It is noteworthy that nitration of 18 occurred preferentially at the 4-position to give 20 as the major product. This is probably because the 4-position is a "*meta*" position in relation to the nitro groups at the 5- and 7-positions and as such is favoured for nitration over the 1-position which is an "*ortho/para*" position.



SCHEME 2

The synthesis of 5,6,8-trinitro-2,3-dimethylnaphthalene (**21**) was achieved by the conversion of the amino group of **17** into a nitro group, via diazotisation and treatment with sodium nitrite (route B of Scheme 2). The trinitro compound (**21**) is of interest since the three nitro groups are in the non-methylated ring, leaving two highly activated sites vacant in the methylated ring. Nitration of **21** in nitric acid/sulphuric acid using the stoichiometric amount of nitric acid for conversion to the tetranitro stage gave a mixture of 1,5,6,8-tetranitro-2,3-dimethylnaphthalene (**22**) and 1,5,7,8-tetranitro-2,3-dimethylnaphthalene (**23**). The nitration of **21** in excess of nitric acid/sulphuric acid yielded 1,4,5,6,8-pentanitro-2,3-dimethylnaphthalene (**24**) as the sole product. Undoubtedly, the formation of this latter compound proceeds via the intermediacy of the tetranitro derivatives **22** and **23** as shown in Scheme 2.

EXPERIMENTAL

Unless otherwise stated, column chromatography was carried out with Merck silica gel (0·05–0·2 mm) using 400 × 20 mm columns, and elution with 1:1 benzene–petroleum (b.p. 60–80°). Mass spectral molecular weights were determined with an AEI MS9 mass spectrometer. NMR spectra were recorded on a Perkin-Elmer R10 spectrometer (tetramethylsilane as internal reference). The structures of the nitration products were assigned from NMR and mass spectra. In particular, the following criteria were used in the assignments from the NMR spectra: (a) a slightly broadened methyl resonance indicated coupling to an *ortho* proton at either the 1- or 4-positions in 2,3-dimethylnaphthalene. (b) a sharp methyl resonance indicated a nitro group in either the 1- or 4-positions.

Nitration of 2,3-*dimethylnaphthalene* (**1**). Nitric acid (*d* 1·42; 1 ml) was added dropwise during 0·5 h to a solution of **1** (1 g) in acetic anhydride (10 ml) maintained in an ice-bath so as to keep the temperature below 10°. The mixture was then maintained at 20° for 2 h, and poured into water (50 ml). The precipitated product was filtered off, washed with water, and dried *in vacuo* to give a pale yellow solid (0·98 g). The first crop from recrystallisation of this solid from petroleum (b.p. 60–80°) gave 1,8-*dinitro*-2,3-*dimethylnaphthalene* (**5**) (0·3 g), m.p. 243–5° (lit,[5] 245°). The remaining crops were combined and column chromatographed to give three fractions. Evaporation to dryness of the first fraction gave 1,4-*dinitro*-2,3-*dimethylnaphthalene* (0·26 g, 17%), m.p. 197°. (Found: C, 58·4; H, 4·2; N, 11·1. $C_{12}H_{10}N_2O_4$ requires C, 58·5; H, 4·1; N, 11·4%); τ ($CDCl_3$) 2·31 (4H, s) and 7·58 (6H, s); *m/e* 246 (M^+). Evaporation of the second fraction to dryness gave 1,5-*dinitro*-2,3-*dimethylnaphthalene* (0·35 g, 22%), m.p. 160°. (Found: C, 58·5; H, 4·6; N, 11·3. $C_{12}H_{10}N_2O_4$ requires C, 58·5; H, 4·1; N, 11·4%); τ ($CDCl_3$) 1·5–2·5 (4H, m), 7·49 (3H, s) and 7·65 (3H, s, broadened); *m/e* 246 (M^+). Evaporation of the third fraction to dryness gave **5** (0·08 g).

Nitration of 1-*nitro*-2,3-*dimethylnaphthalene* (**2**). Nitric acid (*d* 1·42; 0·5 ml) was added dropwise during 0·5 h to a solution of **2** (1 g) in acetic anhydride (10 ml), the temperature being maintained below 10°. After standing at 20° for 1 h, the solution was poured into cold water (50 ml). The precipitate was filtered off, washed with water, and dried *in vacuo* to give a pale yellow solid (0·97 g). The NMR spectrum of a sample of the product showed it to be a 1:1:1 mixture of **5**, **6** and **7**.

Nitration of 5-*nitro*-2,3-*dimethylnaphthalene* (**3**). Nitric acid (*d* 1·42; 0·5 ml) was added dropwise during 0·5 h to a solution of **3** (1 g) in acetic anhydride (10 ml), the temperature being maintained below 10, in an ice-bath. After standing at 20° from 1 h, the solution was poured into water (50 ml). The precipitate was filtered off, washed with water, and dried *in vacuo* to give a pale yellow solid (1·06 g). The NMR spectrum of a sample of the product showed it to be a *ca* 60:40 mixture of **5** and **7**.

Preparation of 1,4,5-*trinitro*-2,3-*dimethylnaphthalene*

(8). A solution of 5 (2 g) in sulphuric acid (*d* 1·84; 30 ml) was prepared, and nitric acid (*d* 1·42; 0·5 ml) added with stirring. The mixture was allowed to stand at 20° for 2 h, and poured on to crushed ice (50 g). The precipitate was filtered off, washed with water, and dried *in vacuo* to give 8 (1·9 g, 81%), m.p. 175°. (Found: C, 49·3; H, 3·3; N, 14·5. $C_{12}H_9N_3O_8$ requires C, 49·5; H, 3·1; N, 14·4%); τ ($CDCl_3$) 1·75–2·3 (3H, m), 7·5 (3H, s) and 7·55 (3H, s); *m/e* 291 (M^+). Using the same procedure, 7 (2 g) gave 8 (2·0 g, 88%). There was no evidence for any other compound in the NMR spectrum of the crude product. Using the same procedure 6 (2 g) gave 8 (1·6 g, 68%). There was no evidence for any other compound in the NMR spectrum of the crude product.

Nitration of 8. Nitric acid (*d* 1·42; 1·5 ml) was added to a solution of 8 (1 g) in sulphuric acid (*d* 1·84; 30 ml). The mixture was stirred for 1 h, and then poured on to crushed ice (50 g). The precipitate was filtered off, and dried *in vacuo* to give a white solid (1·05 g). The NMR spectrum of a sample of the product in $CDCl_3$ showed that it was a *ca* 95:5 mixture of 1,4,5,7-*tetranitro*-2,3-*dimethylnaphthalene* (9) and 1,4,5,8-*tetranitro*-2,3-*dimethylnaphthalene* (10). τ (9) 1·07 and 1·22 (2H, ABq, J_{AB} 2 Hz), 7·37 (3H, s) and 7·44 (3H, s); (10) 1·80 (2H, s) and 7·42 (6H, s). Recrystallisation of the product mixture from glacial acetic acid gave pure 9 (0·97 g, 84%), m.p. 279°. (Found: C, 42·9; H, 2·5; N, 16·2. $C_{12}H_8N_4O_8$ requires C, 42·9; H, 2·4; N, 16·7%); *m/e* 336 (M^+). Evaporation of the mother liquor to dryness gave a residue from which it was not possible to isolate 10, since column chromatography of the mixture using various stationary phases resulted in rapid decomposition in each case.

Preparation of 5,8-*dinitro*-2,3-*dimethylnaphthalene* (12). A soln of 3 (1·1 g) in 95% ethanol (10 ml) was added to a soln of hydroxylamine hydrochloride (3 g) in 95% ethanol (50 ml), and the mixture maintained at 60° whilst a solution of potassium hydroxide (10 g) in methanol (30 ml) was added dropwise, with stirring, during 1 h. The mixture was stirred for a further 2 h, and poured into water (300 ml). The precipitate was filtered off, washed with water and dried. Recrystallisation from 95% ethanol gave 5-*amino*-8-*nitro*-2,3-*dimethylnaphthalene* (11) (0·7 g, 54%), m.p. 188°. (Found: C, 66·4; H, 5·5; N, 13·0%. $C_{12}H_{12}N_2O$ requires C, 66·7; H, 5·6; N, 13·0%). 11 (1 g) was added to a mixture of sulphuric acid (*d* 1·84; 4 ml) and glacial acetic acid (25 ml), and cooled to 5° in an ice-bath. The cooled mixture was added to a soln of sodium nitrite (5 g) in sulphuric acid (*d* 1·84; 5 ml). After standing for 0·5 h, the red diazonium mixture was poured into a mixture of sodium nitrite (10 g), sodium bicarbonate (20 g) and water (200 ml). The brown precipitate (0·7 g) was filtered off, dried, and chromatographed to give 12 (0·06 g, 5%), m.p. 177°. (Found: C, 58·2; H, 4·4; N, 11·3. $C_{12}H_{10}N_2O_4$ requires C, 58·5; H, 4·1; N, 11·4%); τ ($CDCl_3$) 1·82 (2H, s), 2·01 (2H, s) and 7·48 (6H, s, broadened); *m/e* 246 (M^+).

Nitration of 12. A solution of nitric acid (*d* 1·42; 0·25 ml) in sulphuric acid (*d* 1·84; 25 ml) was prepared, and a portion (0·75 ml) added to a soln of 12 (0·03 g) in sulphuric acid (*d* 1·84; 3 ml). The mixture was stirred for 2 h, and poured on to crushed ice (20 g). The precipitate was filtered off, washed with water, and dried *in vacuo* to give 1,5,8-*trinitro*-2,3-*dimethylnaphthalene* (13) (0·025 g, 70%), m.p. 170°. (Found: C, 49·2; H, 3·5; N, 14·1. $C_{12}H_9N_3O_8$ requires C, 49·5; H, 3·1; N, 14·4%); τ ($CDCl_3$) 1·67 (1H, s), 1·88 (2H, s), 7·38 (3H, s, broadened) and 7·48 (3H, s); *m/e* 291 (M^-).

Nitration of 13. Nitric acid (*d* 1·42; 0·05 ml) was added to a soln of 13 (0·02 g) in sulphuric acid (*d* 1·84; 5 ml). The mixture was stirred for 1 h, and poured on to crushed ice (20 g). The precipitate was washed with water and dried *in vacuo* to give 10 (0·02 g, 87%), m.p. 160°. (Found: C, 42·3; H, 2·1; N, 16·1. $C_{12}H_6N_4O_8$ requires C, 42·9; H, 2·4; N, 16·7%); τ ($CDCl_3$) 1·80 (2H, s) and 7·42 (6H, s); *m/e* 336 (M^-).

Preparation of 5,7-*dinitro*-2,3-*dimethylnaphthalene* (18). A soln of 3 (8·5 g) in 95% ethanol (150 ml) was refluxed with hydrazine hydrate (15 ml) in the presence of 10% Palladium on charcoal (0·1 g) for 10 h. Hot filtration, followed by cooling, gave 5-*amino*-2,3-*dimethylnaphthalene* (14) (7·0 g, 96%), m.p. 65°. (Found: C, 84·3; H, 7·5; N, 8·1. $C_{12}H_{13}N$ requires C, 84·2; H, 7·6; N, 8·2%). 14 (7 g) was added to a mixture of glacial acetic acid (25 ml) and acetic anhydride (25 ml). Cooling resulted in the separation of 5-acetamido-2,3-dimethylnaphthalene (15) which was filtered off, washed with water, and dried (8·0 g, 92%), m.p. 162°. (Found: C, 77·7; H, 6·8; N, 6·5. $C_{14}H_{15}NO$ requires C, 77·8; H, 7·0; N, 6·6%). 15 (8 g) was dissolved in acetic anhydride (100 ml), and nitric acid (*d* 1·50; 4 ml) added dropwise, the temp being maintained below 10° in an ice-bath. The mixture was poured into water (500 ml) and the product filtered off and dried. Recrystallisation from 95% ethanol gave 5-*acetamido*-6,8-*dinitro*-2,3-*dimethylnaphthalene* (16) (4·6 g, 41%), m.p. 190°. (Found: C, 55·0; H, 4·2; N, 13·7. $C_{14}H_{13}N_3O_5$ requires C, 55·5; H, 4·3; N, 13·9%). 16 (4·6 g) was refluxed for 16 h in 95% ethanol containing 70% sulphuric acid (15 ml). Cooling and neutralising the reaction mixture with N sodium hydroxide (300 ml) resulted in the precipitation of 5-*amino*-6,8-*dinitro*-2,3-*dimethylnaphthalene* (17), which was filtered off and dried (3·0 g, 76%), m.p. 150°. (Found: C, 55·0; H, 4·2; N, 16·0. $C_{12}H_{11}N_3O_4$ requires C, 55·2; H, 4·2; N, 16·1%). 17 (0·6 g) was added to a mixture of sulphuric acid (*d* 1·84; 2 ml) and glacial acetic acid (15 ml), the resulting mixture cooled to 5° in an ice-bath, and then added to a solution of sodium nitrite (1 g) in sulphuric acid (*d* 1·84; 5 ml). After standing for 0·5 h, the red diazonium solution was poured into a soln of ferrous sulphate (10 g) and ethylene glycol (20 ml) in water (30 ml). The brown precipitate was filtered off, dried and column chromatographed to give 18 (0·08 g, 14%), m.p. 156°. (Found: C, 58·2; H, 4·5; N, 11·3. $C_{12}H_{10}N_2O_4$ requires C, 58·5; H, 4·1; N, 11·4%); τ ($CDCl_3$) 1·10 (2H, s), 1·60 (1H, s), 2·08 (1H, s), 7·43 (3H, s, broadened) and 7·47 (3H, s, broadened) (singlet at 1·10 splits into an ABq on addition of C_6D_6); *m/e* 246 (M^+).

Nitration of 18. Nitric acid (*d* 1·42; 0·12 ml) was added to a soln of 18 (0·5 g) in sulphuric acid (*d* 1·84; 20 ml). The mixture was stirred at 20° for 2 h, and then poured on to crushed ice (50 g). The precipitate was filtered off, washed with water, and dried *in vacuo* to give a pale yellow solid (0·4 g). Column chromatography of the solid yielded two fractions. Evaporation of the first fraction to dryness gave 1,5,7-*trinitro*-2,3-*dimethylnaphthalene* (19) (0·095 g, 16%), m.p. 169° (yellow needles). (Found: C, 49·3; H, 3·5; N, 14·6. $C_{12}H_9N_3O_8$ requires C, 49·5; H, 3·1; N, 14·4%); τ ($CDCl_3$) 1·05 and 1·21 (2H, ABq, J_{AB} 2 Hz), 1·46 (1H, s), 7·35 (3H, s, broadened) and 7·54 (3H, s); *m/e* 291 (M^+) (base peak at *m/e* 291). Evaporation of the second fraction to dryness gave 1,6,8-*trinitro*-2,3-*dimethylnaphthalene* (20) (0·232 g, 39%), m.p. 178° (white crystals). (Found: C, 49·6; H, 3·3; N, 14·7. $C_{12}H_9N_3O_8$ requires C, 49·5; H, 3·1; N, 14·4%); τ ($CDCl_3$) 1·05 and 1·21 (2H, ABq, J_{AB} 2 Hz), 1·84 (1H, s), 7·35

(3H, s, broadened), 7·46 (3H, s); *m/e* 291 (M^+) (base peak at *m/e* 245).

Preparation of 5,6,8-*trinitro*-2,3-*dimethylnaphthalene* (**21**). **17** (0·9 g) was added to a mixture of sulphuric acid (*d* 1·84; 1·5 ml) and glacial acetic acid (15 ml), and cooled to 5° in an ice-bath. The mixture was added to a soln of sodium nitrite (1 g) in sulphuric acid (*d* 1·84; 4 ml), and allowed to stand for 0·5 h. The red diazonium solution was poured into a mixture of sodium nitrite (7 g), sodium bicarbonate (15 g), and water (150 ml) to give a buff coloured precipitate, which was filtered off and dried. The product (0·3 g) was chromatographed on a column of silica gel (350 × 20 mm) using benzene as eluent to give **21** (0·15 g, 18%), m.p. 152°. (Found: C, 50·2; H, 3·6; N, 13·9. $C_{12}H_9N_3O_6$ requires C, 49·5; H, 3·1; N, 14·4%); τ ($CDCl_3$) 1·22 (1H, s), 1·61 (1H, s), 2·35 (1H, s), 7·40 (3H, s, broadened) and 7·45 (3H, s, broadened); *m/e* 291 (M^+).

Nitration of **21**. A solution of nitric acid (*d* 1·42; 2·5 ml) in sulphuric acid (*d* 1·84; 25 ml) was prepared, and a portion (0·4 ml) added to a soln of **21** (0·2 g) in sulphuric acid (*d* 1·84; 6 ml). The mixture was maintained at 35° for 1 h, and then poured on to crushed ice (10 g). The resulting precipitate was filtered off, washed with water, and dried *in vacuo* to give a white solid (0·2 g). Elemental analysis showed that the product was a mixture of tetranitro-2,3-dimethylnaphthalenes. (Found: C, 42·9; H, 2·3; N, 16·3. $C_{12}H_8N_4O_8$ requires C, 42·9; H, 2·4; N, 16·7%). The NMR spectrum of a sample of the product in $CDCl_3$ showed that it was a *ca* 70:30 mixture of 1,5,7,8-*tetranitro*-2,3-*dimethylnaphthalene* (**23**) and 1,5,6,8-*tetranitro*-2,3-*dimethylnaphthalene* (**22**); τ (**23**) 1·23 (1H, s), 2·18 (1H, s), 7·35 (3H, s, broadened) and 7·43 (3H, s); τ (**22**) 1·40 (1H, s), 1·60 (1H, s), 7·43 (3H, s, broadened) and 7·54 (3H, s). All attempts to separate the mixture by column chromatography failed due to decomposition of the products on the various stationary phases used.

Nitric acid (*d* 1·42; 1 ml) was added to a soln of **21** (0·13 g) in sulphuric acid (*d* 1·84; 10 ml). The mixture was stirred at 50° for 2 hr, then poured on to crushed ice (50 g). The resulting precipitate was filtered off, washed with water, and dried *in vacuo* to give 1,4,5,6,8-*pentanitro*-2,3-*dimethylnaphthalene* (**24**) (0·05 g, 34%), m.p. 175°. (Found: C, 37·2; H, 2·4; N, 17·8. $C_{12}H_7N_5O_{10}$ requires C, 37·8; H, 1·8; N, 18·4%); τ (CD_3COCD_3) 0·81 (1H, s), 7·29 (3H, s) and 7·36 (3H, s); *m/e* 381 (M^+).

Acknowledgements—We thank Dr. I. Dunstan and Mr. J. A. Bell of the Explosives Research and Development Establishment, Ministry of Defence, for discussions.

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Studies on Nitroaromatic Compounds. Part VI.[1] Synthesis of Polynitro-1,5- and -1,8-dimethylnaphthalenes

By Stephen R. Robinson, Brian C. Webb, and Clifford H. J. Wells,* School of Chemical and Physical Sciences, Kingston Polytechnic, Kingston-upon-Thames, Surrey

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Studies on Nitroaromatic Compounds. Part VI.[1] Synthesis of Polynitro-1,5- and -1,8-dimethylnaphthalenes

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The nitration of 1,5- and 1,8-dimethyl-4-nitronaphthalene has been studied in different media and a number of new polynitro-1,5- and -1,8-dimethylnaphthalenes have been prepared.

MANY of the explosives used in space research are required to be thermally stable and of low volatility since they may have to be sterilised by thermal means prior to transportation in spacecraft [2] and may be subjected to high temperature and low pressure under conditions of use.[3] 2,2',4,4',6,6'-Hexanitrostilbene has found wide application as an explosive for use in space [2,3] and is prepared for such purpose by treatment of 2,4,6-trinitrotoluene with base.[4] Since polynitro-1,5- and -1,8-dimethylnaphthalenes are structurally similar to polynitrotoluenes, they are of interest as possible intermediates in the preparation of thermally stable explosives of low volatility. The nitration of 1,5- and 1,8-dimethylnaphthalene has been relatively little studied, and only mononitro-derivatives have been reported to date.[5] In view of this, we have investigated the nitration of 1,5- and 1,8-dimethyl-4-nitronaphthalene [(I) and (VI)] in relation to the preparation of polynitro-derivatives. The conditions used for the nitrations are shown in

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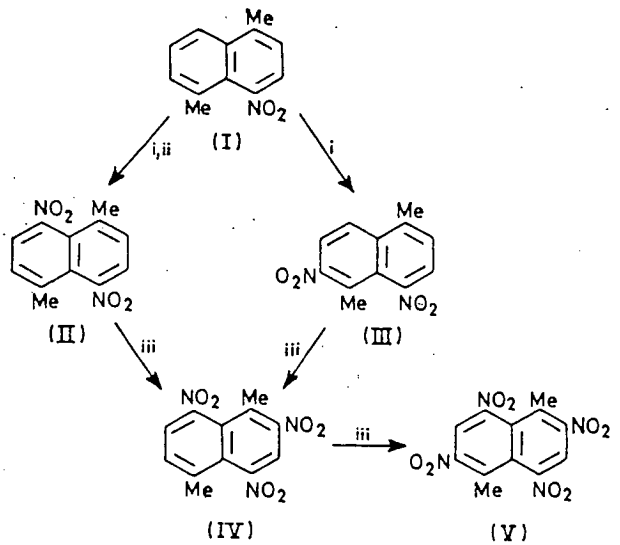
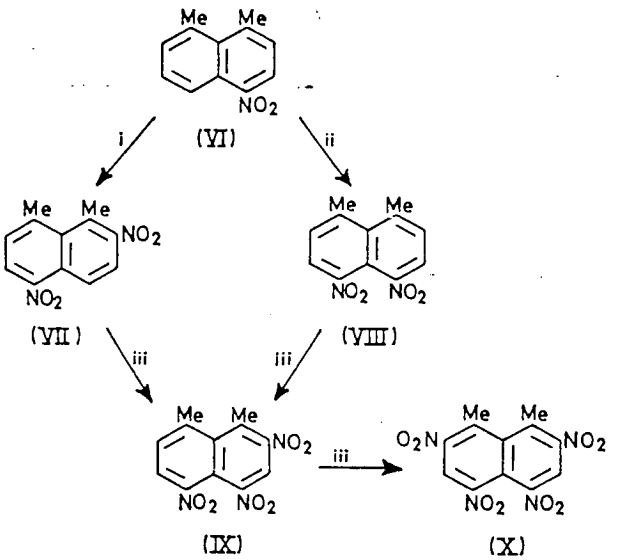
Schemes 1 and 2, as are the new compounds (II)—(V) and (VII)—(X) which have been synthesised.



SCHEME 1 Reagents: i, HNO_3–Ac_2O; ii, fuming HNO_3–$(CH_2Cl)_2$; iii, HNO_3–H_2SO_4

EXPERIMENTAL

Details are available as Supplementary Publication No. SUP 21104 (6 pp.).*



SCHEME 2 Reagents as Scheme 1

We thank the Ministry of Defence for financial support and for a maintenance grant (to B. C. W.).

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

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RESEARCH NOTE

Electronic spectra of nitro- and polynitro-acenaphthenes and of nitro- and polynitro-1,8-dimethylnaphthalenes

(*Received* 29 *April* 1974)

Abstract—The electronic absorption spectra of twelve nitro- and polynitro-acenaphthenes and of five nitro- and polynitro-1,8-dimethylnaphthalenes have been measured and discussed.

THE ELECTRONIC spectra of nitro and polynitro aromatic compounds have not been studied to any extent, with the exception of the nitro-derivatives of benzene [1–10]. A number of studies have been carried out, however, on the electronic spectra of conjugated nitro olefins [11–13]. As part of a study on the chemistry of nitroaromatic compounds we have synthesised a number of new polynitroacenaphthenes [14] and polynitro-1,8-dimethylnaphthalenes [15] and the main features of the ultraviolet absorption spectra of these compounds and of mononitro derivatives of acenaphthene and 1,8-dimethylnaphthalene are given in Table 1.

The compounds listed in Table 1 exhibit three main absorption bands in the wavelength range 250–400 nm. This is similar to the spectrum of naphthalene where the bands at 221, 286 and 312 nm correspond to $^1B_b \leftarrow {}^1A$, $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ transitions respectively [16]. Information on structure-wavelength and structure-intensity correlations is limited for band I in the present set of spectra on account of solvent absorption but the band does show a trend of a blue shift and intensification as the degree of substitution by nitro groups increases. Likewise, band II exhibits a hypsochromic effect and a hyperchromic effect with increasing substitution. There are, however, notable differences in the extinction coefficients for band II within the groups of dinitroacenaphthene, trinitroacenaphthene and tetranitroacenaphthene derivatives. Thus, in situations where there is steric interaction between *ortho* substituted nitro groups, as in 4,5-dinitroacenaphthene, and between *peri* substituted nitro groups, as in 3,5,6-trinitroacenaphthene, the molar extinction coefficient is considerably less than that for the non-sterically hindered derivatives within the group. It is also of interest that the band II extinction coefficients for 2,5-dinitro-1,8-dimethylnaphthalene ($\varepsilon = 5620$) and for 2,4,5,7-tetranitro-1,8-dimethylnaphthalene ($\varepsilon = 23{,}400$) are considerably lower than the values for their respective acenaphthene

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Table 1. Wavelengths (nm) and molar extinction coefficients* (1 mol^{-1} cm^{-1}) of main bands in the electronic absorption spectra of nitroacenaphthenes and nitro-1,8-dimethylnaphthalenes in chloroform solution†

Compound	Band I	Band II	Band III
3-NA‡	272(29,700)	298(8550)	374(5720)
4-NA	274(30,100)	303(7230)	374(3560)
5-NA	262(15,100)	314(2510)	376(7220)
4-NDMN‡	256(10,000)	~290(~2500)	364(3800)
3,6-DiNA	<250§	288(16,000)	351(8890)
4,6-DiNA	259(25,400)	294(12,500)	375(9180)
5,6-DiNA	<250§	—‖	349(8420)
3,7-DiNA	268(43,600)	299(11,500)	385(5690)
4,5-DiNA	272(16,500)	305(4000)	376(2440)
2,5-DiNDMN	<250§	296(5620)	343(4670)
4,5-DiNDMN	<250§	—¶	342(7200)
3,5,6-Tri NA	<250§	278(4380)	345(1930)
3,5,8-Tri NA	—**	277(13,300)	351(4070)
2,4,5-Tri NDMN	<250§	—‖	331(5620)
3,5,6,7-Tetra NA	—**	271(21,000)	360(5470)
3,5,6,8-Tetra NA	—**	269(41,600)	364(11,100)
2,4,5,7-Tetra NDMN	—**	264(23,400)	328(7900)

* Extinction coefficients are shown in parenthesis.

† Chloroform was used as solvent on account of the insolubility of many of the compounds in nonpolar solvents.

‡ The symbols NA and NDMN refer to nitroacenaphthene and nitro-1,8-dimethylnaphthalene respectively.

§ Band maximum obscured by solvent absorption.

‖ Inflection.

¶ Obscured by band I.

** Band I totally obscured.

structural counterparts viz. 3,6-dinitroacenaphthene (ε = 16,000) and 3,5,6,8-tetranitroacenaphthene (ε = 41,600). This probably reflects the greater steric interaction between the alkyl substituents and the adjacent nitro group(s) in the dimethylnaphthalene derivatives.

Band III in the spectra may be assigned as arising from transitions associated with the substituent nitro groups, and according to NAGAKURA [5] these transitions may be of the intramolecular charge-transfer type. It is noteworthy that for those dinitroacenaphthenes where the nitro groups are effectively *meta* to each other, viz. the 3,6- and 5,6-derivatives, the band III maxima are blue shifted relative to the maxima for those dinitroacenaphthenes in which the nitro groups are effectively *ortho/para* positioned viz. the 4,6-, 3,7- and 4,5-derivatives. *Meta* substitution of the nitro groups allows resonance stabilisation of the ground state and, consequently, greater energy is required for electron promotion to an upper electronic state as compared to the situation for *ortho/para* substitution.

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Mass Spectroscopy, Isotopes and Ionisation Potentials

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Two of the most significant discoveries of physical science arose as a result of mass spectroscopic studies; these being the discovery of isotopes and of the mass defect in elements. Although mass spectroscopy is still used for research in the physical sciences, it is most widely noted nowadays for its range of applications to problems in the chemical sciences, of which one of the most important is in the elucidation of the structure of compounds.

MASS SPECTROSCOPY is concerned with the analysis of ions formed from atoms or molecules. One method for ionising atoms or molecules is to bombard the gaseous sample with a beam of electrons. This is brought about in mass spectroscopy by injecting the sample into an evacuated chamber (see Figure 1) where a heated metal filament emits electrons which are accelerated to high energy across the chamber by means of an electron trap held at a positive potential. In the case of a molecule (m), say, collision with the electron beam will result in an electron being ejected from the molecule to give a positively charged ion, termed the *molecular ion* (m^+). In many cases the molecular ion formed is highly energetic and fragments to give ions of lower mass (m_1^+, m_2^+, - - -). The ions formed are characteristic of the parent molecule and can be used for the purposes of structure identification.

The ions once formed are accelerated using a negative potential, separated according to their mass-to-charge (m/e) ratio, and the relative abundances of ions of different m/e value measured. The acceleration and separation processes can be illustrated conveniently by means of the mechanical model shown in Figure 2. If a series of wooden balls of different sizes, and hence mass, but all having the same sized iron core, are allowed to roll down the slope, then they will have a kinetic energy at the bottom which is dependent upon their mass. The magnet sited at the bottom of the slope exerts the same attraction on each ball but since the deflection produced will depend upon the mass of the ball (the light ones being deflected most) the balls of different mass will follow separate paths, as shown in Figure 2.

In mass spectroscopy the ions of different m/e value are induced to follow different paths by applying a strong magnetic field (about 3000 Gauss) at right angles to their direction of flight in the spectrometer. Under such circumstances, ions follow a curved flight path governed by the equation

$$\frac{m}{e} = \frac{B^2 r^2}{2V}$$

where B is the strength of the magnetic field, r is the radius of curvature of the ion path, and V is the accelerating potential. If the values of B and V are held constant, the ions of different m/e values will follow flight paths having different radii of curvature and the ion beam entering the magnetic field will become separated into beams of ions of different m/e value (see Figure 3). In a *mass spectrograph* the ion beams separated in this way impinge onto a photographic plate where the images formed can be related to the relative abundance of the ions in each of the beams. In a *mass spectrometer* the radii of curvature of the ion paths are altered by either varying the accelerating potential V or the magnetic field strength B so that each ion beam passes successively through the entrance slit of an

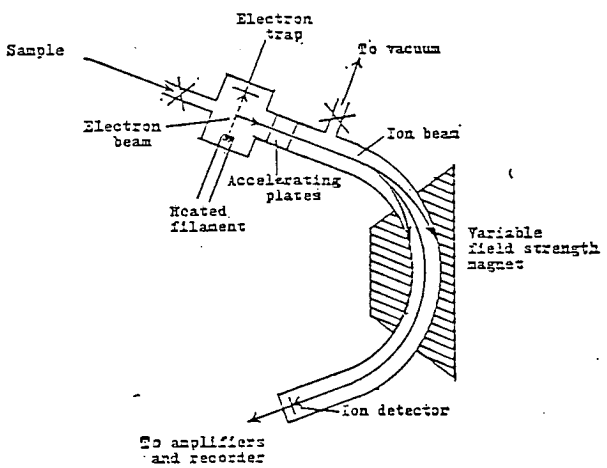

Figure 1 — Schematic diagram of a mass spectrometer.

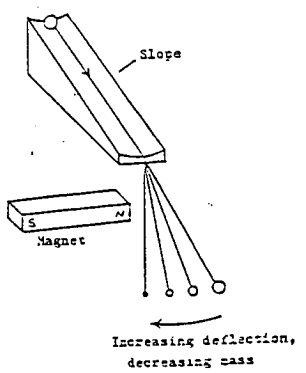

Figure 2 — Mechanical model simulating acceleration and magnetic separation of ions.

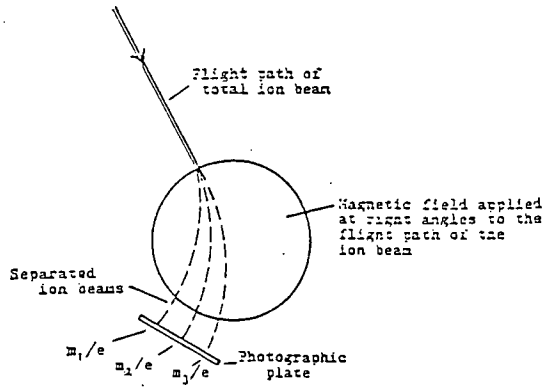

Figure 3 — Ion separation and detection in a mass spectrograph.

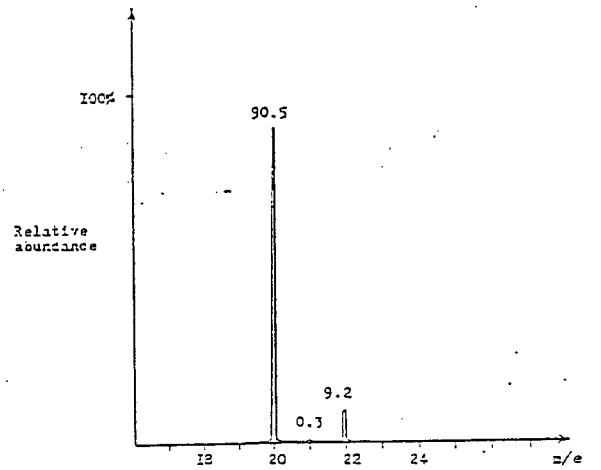

Figure 4 — Partial mass spectrum of neon showing peaks due to singly charged ions.

ion detector where the relative abundance of the ions in each beam is recorded as an electrical signal. A typical modern mass spectrometer is shown schematically in Figure 1, where the relative disposition of the ion source, ion accelerator, ion separator and ion detector can be seen.

Isotopes

The mass spectrum that would be obtained for neon from a spectrometer as described above is shown in Figure 4. Neon has three isotopes, $^{20}_{10}Ne$, $^{21}_{10}Ne$ and $^{22}_{10}Ne$, and since they are of different mass, the ions formed from them will be of different m/e value and hence give rise to three ion beams in the spectrometer and hence three peaks in the spectrum. Ions formed from atoms, unlike those from molecules, cannot fragment further and hence there are no other peaks in the spectrum of neon due to the singly charged species. However, low intensity peaks occurring from the corresponding doubly charged species are observed. The heights of the peaks are proportional to the number of ions in each beam and hence it can be deduced from the mass spectrum that the $^{20}_{10}Ne$, $^{21}_{10}Ne$ and $^{22}_{10}Ne$ isotopes are present in neon in the ratio of 10:0.03:1. Thus the atomic weight of neon can be calculated to be 20.2, in agreement with the accepted value.

The discovery of the existence of isotopes was made by J. J. Thompson in 1912 when by studying the effect of electric and magnetic fields on the "positive rays" produced in neon discharge tubes, he was able to demonstrate the presence of the two most abundant isotopes of neon. These findings were later extended using a more conventional mass spectrograph when the occurrence of three isotopes of neon was demonstrated and their relative proportions determined. F. W. Aston was able to show that the masses of individual isotopes (nuclides) when measured on the atomic weight scale actually differed from whole numbers. Precise measurements of relative atomic mass by mass spectrometry have subsequently shown that the masses of nuclides are not exactly equal to the sum of the individual masses of the component protons, neutrons and electrons. The difference in masses is termed the *mass defect* and is a measure of the binding energy of the nucleus as governed by Einstein's relationship $E = mc^2$. Thus mass spectroscopic studies provided experimental evidence for Einstein's special theory of relativity.

Ionisation Potential and the Periodic Table

The efficiency of production of positive ions in a mass spectrometer is a function of the energy of the ionising medium. When a beam of electrons is used for ionisation of the sample, the kinetic energy of the electrons in the beam is changed by varying the positive potential on the electron trap in the ionisation chamber (Figure 1). If the intensity of a beam of ions of particular m/e value reaching the ion detector is monitored as the electron beam energy is varied then a plot such as shown in Figure 5 is observed. If it is assumed that the energy gained by an atom or molecule upon electron impact is equal to the energy of the electron beam, then the energy required to remove an electron from the atom or molecule (termed the *ionisation potential*) is given by the value of the electron beam energy at which the relevant ions are first detected (see Figure 5). The ionisation potentials of a number of atomic species (Ce, Er, Nd, Tb, Th, U) have been obtained by mass spectral methods although the majority of atomic ionisation potentials have been measured by other spectroscopic methods.

The values of the first ionisation potential of the elements are of interest since a plot of these values against the atomic number clearly shows the existence of shells in the arrangement of electrons in an element. The plot of first ionisation potential against atomic number is shown in Figure 6 where it can be seen that minima occur for the alkali metal elements (Li, Na, K, Rb, Cs) and maxima for the noble gas elements (He, Ne, Ar, Kr, Xe). These results are readily explainable on the basis that a relatively low amount of energy is required to remove the single unpaired electron in the outermost shell of the alkali metal elements, whilst a relatively high energy is required to remove an electron from the completely filled outermost shell of the noble gas elements. The pattern of the values for the first ionisation potentials between the minima and maxima on the plot gives information on the arrangement of electrons in the electronic sub-shells of the elements. For example, there is an increase in ionisation potential for the elements going from boron to neon corresponding to the filling of the 2p sub-shell. The somewhat anomalous position of nitrogen arises as a consequence of the 2p shell of this element being half-filled, the enhanced ionisation potential reflecting the stability of a half-filled sub-shell.

The stability of a completely filled shell is also demonstrated by the values for the ionisation potentials for successive removal of electrons from any element. Thus, in general, the values increase regularly for an element as the valency electrons are successively removed until a shell is emptied, whence a very large increase is observed for

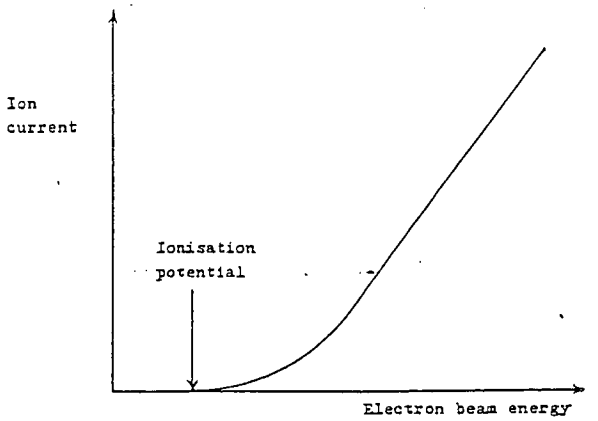

Figure 5 — Ionisation potential plot.

$M(g) - M^{+}(g) + e$

kJ g-atom^{-1}

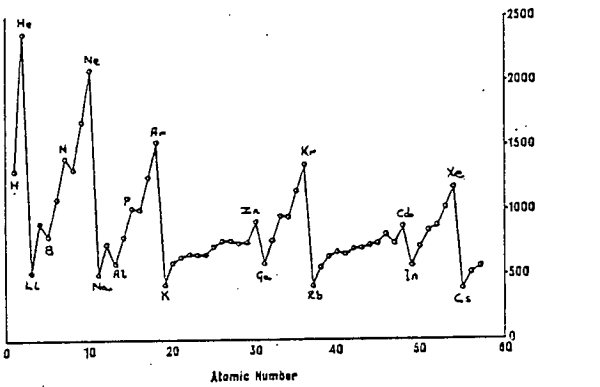

Figure 6 — Variation of the first ionisation potential with atomic number.

the removal of an electron from the next lower-lying filled shell.

For example, beryllium has first and second ionisation potentials of 898.8 and 1755.2 kJg-atom^{-1} corresponding to removal of the two 2s electrons, while the subsequent removal of a ls electron requires an energy of 14,851.76 kJg-atom^{-1}. Examination of the values for the ionisation potentials of Na, Mg, Al, Si and P given in the Table shows the marked increase to occur after removal of one, two, three, four and five electrons respectively. Such large increases are reflected in the effective upper valency limits of these elements.

TABLE

Element	Ionisation potential (kJg-atom^{-1})					
	1st.	2nd.	3rd.	4th.	5th.	6th.
Na	495.9	4.563.7				
Mg	737.1	1.447.3	7.728.4			
Al	577.0	1.813.9	2.740.2	11.578.1		
Si	786.4	1.572.7	3.232.2	4.351.4	16.112.8	
P	1,061.4	1,900.7	2,913.8	4.959.3	6.271.5	21,226.5

Chemistry and Industry, 21 June 1975

Base-induced coupling of 4-nitro-1,5- and -1,8-dimethylnaphthalenes

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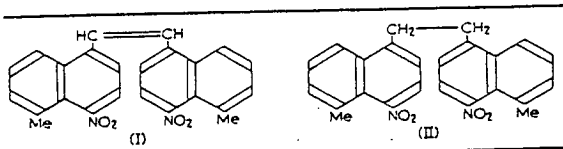
Dimerisation of 2,4,6-trinitrotoluene (TNT) under alkaline conditions yields 2,2',4,4',6,6'-hexanitrostilbene (HNS) in good yield,[1] this latter compound being of importance as a thermally stable explosive suitable for use in space research.[2,3] Knowledge of this reaction prompted an investigation of the action of base on 4-nitro-1,5-dimethylnaphthalene and 4-nitro-1,8-dimethylnaphthalene with a view to obtaining coupled products which would have the potential for further nitration to polynitro compounds analagous in structure to HNS.

The reaction of potassium hydroxide in methanol with 4-nitro-1,5-dimethylnaphthalene gave 4,4'-dinitro-5,5'-dimethyl-*bis*-1,2(1-naphthyl)ethene (I) and 4,4'-dinitro-5,5'-dimethyl-*bis*-1,2(1-naphthyl)ethane (II) as initial products, while prolonged reaction yielded 4-methoxy-5-methyl-1-naphthaldehyde (III) as sole product. The reactions were performed as follows. To a solution of 4-nitro-1,5-dimethylnaphthalene (1g) in methanol (50cm³) was added 30 per cent potassium hydroxide in methanol (30cm³), and the solution stirred for 12h at 20°. The precipitated yellow solid (0·6g) was filtered off, and recrystallised from nitrobenzene to give compound (I), (0·55g), mp 282°, n.m.r. spectrum ($CDCl_3$), τ 2·2 – 2·6 (6H,*m*) and τ 7·45 (3H,*s*), mass spectrum, *m/e* 398 (M^+). The mother liquor was evaporated to dryness, the residue extracted with benzene, and the extract run on a silica gel t.l.c. plate (0·3mm; 200 × 200mm) using 1:1 benzene/light petroleum (bp 60–80°) as eluent. The band at R_f 0·89 was extracted with methanol, and evaporated to dryness to give compound (II) (0·01g), mp 220°, n.m.r. spectrum ($CDCl_3$), τ 2·3 – 2·6 (5H,*m*), 6·55 (2H,*s*) and 7·65 (3H,*s*); mass spectrum, *m/e* 400 (M^+).



Sampling (5cm³) of the initial reaction mixture at hourly intervals, drowning out in hydrochloric acid (2N; 25cm³), and analysing the precipitated products by n.m.r. spectral measurements showed the disappearance of compounds (I) and (II) with time and the appearance of compound (III). After 24h the precipitated product contained only compound (III), mp 73°, n.m.r. spectrum ($CDCl_3$), τ −0·1 (1H,*s*), 0·7 (1H,*s*), 2·3 – 2·6 (2H,*m*), 2·10 and 3·10 (2H, AB_q, J_{AB} 9Hz), 6·0 (3H,*s*) and 7·15 (3H,*s*); mass spectrum *m/e* 200 (M^+).

The action of potassium hydroxide in methanol-tetrahydrofuran on 4-nitro-1,8-dimethylnaphthalene yielded 4,4'-dinitro-8.8'-dimethyl-1,2-*bis*-(1-naphthyl)ethene (IV), 4,4'-dinitro-8.8'-dimethyl-1,2-*bis*-(1-naphthyl)ethane (V), and 4-methoxy-8-methyl-1-naphthaldehyde (VI) in a similar fashion to the reaction of base with 4-nitro-1,5-dimethylnaphthalene. Spectral properties are in agreement with the assigned structures: (IV) – n.m.r. spectrum, ($C_6D_5NO_2$) τ 2·3 – 2·8 (overlapped by solvent) and 7·03 (*s*); mass spectrum, *m/e* 398 (M^+); (V) – n.m.r. spectrum ($CDCl_3$), τ 2·0 – 3·0 (5H,*m*), 6·31 (2H,*s*) and 7·10 (3H,*s*); mass spectrum, *m/e* 400 (M^+); (VI) – n.m.r. spectrum ($CDCl_3$), τ −0·1 (1H,*s*), 1·6 – 2·7 (3H,*m*), 1·90 and 3·14 (2H, AB_q, J_{AB} 9Hz), 5·95 (3H,*s*) and 7·20 (3H,*s*).

All the new compounds gave satisfactory elemental analyses.

The Ministry of Defence is thanked for financial support of this work.

Received 16 January 1975

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Studies on Nitroaromatic Compounds. Part VII.[1] A Nuclear Magnetic Resonance Study of the Reaction of [$^2H_3$]Methoxide Ion with Some Polynitrodimethylnaphthalenes

By **Stephen R. Robinson, Brian C. Webb,** and **Clifford H. J. Wells,*** School of Chemical and Physical Sciences, Kingston Polytechnic, Penrhyn Road, Kingston upon Thames, Surrey

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Studies on Nitroaromatic Compounds. Part VII.[1] A Nuclear Magnetic Resonance Study of the Reaction of [$^2H_3$]Methoxide Ion with Some Polynitrodimethylnaphthalenes

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The interaction of 1,8-dimethyl-2,4,5,7-tetranitro- (I), 1,5-dimethyl-2,4,6,8-tetranitro- (II), and 1,5-dimethyl-2,4,8-trinitro-naphthalene (III) with [$^2H_3$]methoxide ion in [$^2H_6$]dimethyl sulphoxide has been investigated by ^1H n.m.r. spectroscopy. The major initial reaction is proton abstraction from a methyl group of (I)—(III) to give a resonance stabilised benzyl-type anion. The anions from (I) and (III) are stable, whereas the anion from (II) undergoes isomerisation to give a stable product. The anion from (III), unlike those from (I) and (II), can react with [$^2H_3$]methoxide ion to give a dianionic species. In the case of (I), addition of base to a nuclear position in the parent nitro-compound competes with proton abstraction.

THE reactions of nitroaromatic compounds with base are well documented [2-5] and, of these, the reactions of 2,4,6-trinitrotoluene (TNT) with both weak and strong base have received considerable attention. In a number of systems the reaction of TNT with base has been postulated as proceeding *via* the intermediacy of the 2,4,6-trinitrobenzyl anion (TNT^-).[6-10]

Whereas in many cases, ^1H n.m.r. spectroscopy has provided direct evidence in establishing the structures of intermediates and products in the reactions of alkoxide with nitroaromatic compounds,[2-5] it has not proved possible to obtain n.m.r. spectra relating to the reaction of alkoxide with TNT, owing probably to the presence of free radicals in these systems.[4,11] Hence it has not been possible to gain direct structural evidence for the existence of the TNT^- anion. We have investigated the reaction of [$^2H_3$]methoxide ion with some polynitrodimethylnaphthalenes which are structurally related to TNT, and now report on n.m.r. evidence for the formation of benzyl-type anions in the systems studied.

RESULTS AND DISCUSSION

As can be seen from Figure 1, there are notable differences between the ^1H n.m.r. spectrum of 1,8-dimethyl-2,4,5,7-tetranitronaphthalene (I) in [$^2H_6$]dimethyl sulphoxide and the n.m.r. spectrum of a 1 : 1 mixture of (I) and sodium [$^2H_3$]methoxide in the same medium. The most noticeable effect of addition of sodium [$^2H_3$]-methoxide is the splitting of the aromatic proton resonance of (I) into two resonances at τ 1.43 and 1.72, the halving in relative intensity of the methyl proton resonance at τ 7.31, and the appearance of two new resonances at τ 3.84 and 4.69 [see Figure 1(b)]. The integral ratio of these resonances (from low to high field) is 1 : 1 : 1 : 1 : 3. The broad resonance at τ *ca.* 6.0 and the multiplet resonance centred at 7.50 were present in all spectra after addition of base and can be assigned to CD_3OH and CD_2HSOCD_3 respectively. Other features are the appearance of somewhat weaker resonances close to τ 7.0 and 8.0 and in the region τ 1—2.

The spectrum of Figure 1(b) indicates that reaction with [$^2H_3$]methoxide occurs at a methyl group of (I) and that this involves loss of a proton to give a structure in which the remaining two protons resonate in the midfield

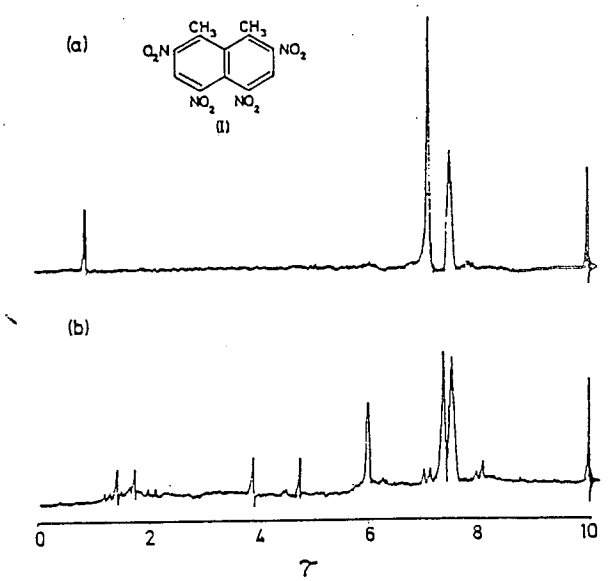

FIGURE 1 ^1H N.m.r. spectra of 1,8-dimethyl-2,4,5,7-tetranitronaphthalene in [$^2H_6$]dimethyl sulphoxide containing sodium [$^2H_3$]methoxide; mole ratio [CD_3O^-] : [nitroaromatic] is (a) 0.0 and (b) 1.0

region of the spectrum. The main features of the spectrum can be explained in terms of a resonance stabilised benzyl-type anion of which two canonical forms (IV) and (V) are shown in Scheme 1. The observation of two resonances in the midfield region indicates that structure (V), and other similar canonical forms involving charge

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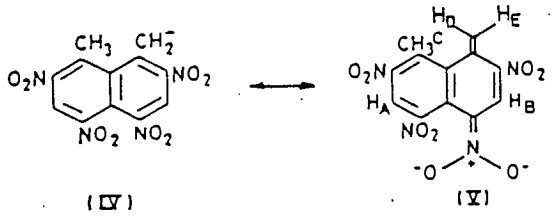
localisation at a nitro-group, represent the charge distribution in the anion more closely than structure (IV). Thus the resonances at τ 1.43, 1.72, and 7.31 can be



(IV) (V)

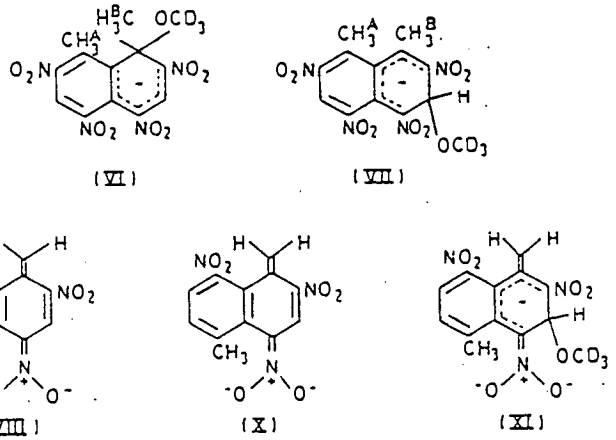
SCHEME 1

assigned to protons H_A, H_B, and H_O of anion (V) respectively, while the resonances at τ 3.84 and 4.69 can be assigned to protons H_D and H_E. It is not possible to assign unambiguously the resonance for H_D and H_E as their relative chemical shifts will depend upon the orientation of the 2-nitro-group and the associated shielding cone with respect to the aromatic ring system. The absence of observable coupling between the geminal protons H_D and H_E is consistent with the n.m.r. spectra of other compounds in which the exocyclic olefinic group is part of a conjugated system.[12,13] Further evidence of hydrogen abstraction having occured from (I) was obtained by adding a sample exhibiting the n.m.r. spectrum of Figure 1(b) to deuteriochloric acid–heavy water whence 1,8-dimethyl-2,4,5,7-tetranitro[^{2}H]naphthalene was precipitated.

The signals in the spectrum of anion (V) decreased in intensity with time and were not detectable after 24 h; no new signals were detectable however. The change in spectrum does not arise because of reaction of anion (V) with [$^2H_3$]methoxide ion since addition of two equivalents of sodium [$^2H_3$]methoxide to a sample exhibiting the spectrum of anion (V) did not cause any alteration in the spectrum.

The weak resonances in the spectrum of Figure 1(b) most probably arise from the 1 : 1 adducts (VI) and (VII) formed by σ-addition of the [$^2H_3$]methoxide ion at the C-1 and -3 positions of (I) respectively. On this basis, the resonances at τ 6.96 and 7.08 can be assigned to the H_A protons of (VI) and (VII), whilst the resonances at τ 7.92 and 8.04 can be assigned to the H_B protons of (VI) and (VII). The weak singlet resonances in the region of τ 1—2 may be attributed to the aromatic protons of (VI) and (VII). The sum of the integrals for the H_A resonances of (VI) and (VII) amounted to *ca.* 15% that of the integral for the H_O protons of (V). It is thus apparent that the reaction of [$^2H_3$]methoxide ion with (I) involves competitive proton abstraction and σ-addition processes, and that under the conditions employed in the present study, compound (I) undergoes *ca.* 85% methyl proton abstraction to 15% σ-addition. This contrasts to the reaction of methoxide with 2,4,6-trinitroaniline where, in a 1 : 1 methanol–dimethyl sulphoxide solvent system, the nitroaromatic compound undergoes *ca.* 20% NH proton abstraction and 80% σ-addition.[11,14]

The effect of sodium [$^2H_3$]methoxide on the n.m.r. spectrum of 1,5-dimethyl-2,4,6,8-tetranitronaphthalene-(II) is shown in Figure 2. The spectrum of Figure 2(b), obtained shortly after addition of one equivalent of sodium [$^2H_3$]methoxide, is similar to that of Figure 1(b) both in terms of chemical shift positions and relative integral ratios of the observed resonances. Thus it would appear that a resonance stabilised benzyl-type anion (VIII) is formed by proton abstraction from (II).



(VI) (VII) (VIII) (X) (XI)

Unlike (V), the anion (VIII) is not stable and within 30 min the spectrum of (VIII) is replaced by that shown in Figure 2(c). In this latter spectrum, the olefinic resonances of (VIII) in the midfield region have been replaced by two resonances of the same intensity in the low field region. With regard to this, it is interesting to note that a downfield shift has been observed for the amino protons in 2,4,6-trinitroaniline on reaction of 2,4,6-trinitroaniline with base.[15] This shift was ascribed to

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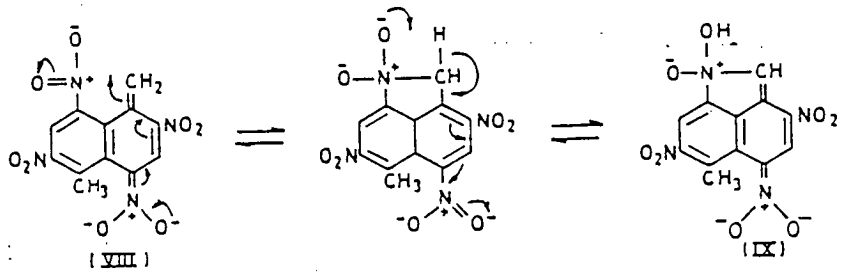
increased hydrogen bonding between the amino-protons and the adjacent nitro-groups in the anion as compared to that in the parent molecule. The time scale of the present process excludes hydrogen bonding as the cause of the change but indicates, instead, some form of chemical reaction. The disappearance with time of the olefinic resonances of (VIII), coupled with the observation that anion (V) is stable and does not react in this way, suggests that the reaction proceeds *via* the nitro-group at the 8-position. A reaction product of structure (IX) could account for the observed n.m.r. spectrum. The formation of this product can be rationalised in terms of the mechanism tentatively proposed in Scheme 2. As might be expected, the reaction sequence (II) ⟶ (VIII) ⟶ (IX) is reversed under acid conditions. Thus, addition of a solution exhibiting the n.m.r. spectrum of Figure 2(C) to deuteriochloric acid–heavy water gave 1,5-dimethyl-2,4,6,8-tetranitro[^{2}H]naphthalene.



SCHEME 2

Reaction of sodium [$^2H_3$]methoxide with 1,5-dimethyl-2,4,8-trinitronaphthalene (III) in 1 : 1 mole ratio gives the n.m.r. spectrum shown in Figure 3(b). It is apparent that an anion of similar structure to (V) and (VIII) is formed. Comparison of this spectrum with that of (III) in Figure 3(a) shows clearly that the olefinic resonances of the anion are derived from one of the methyl

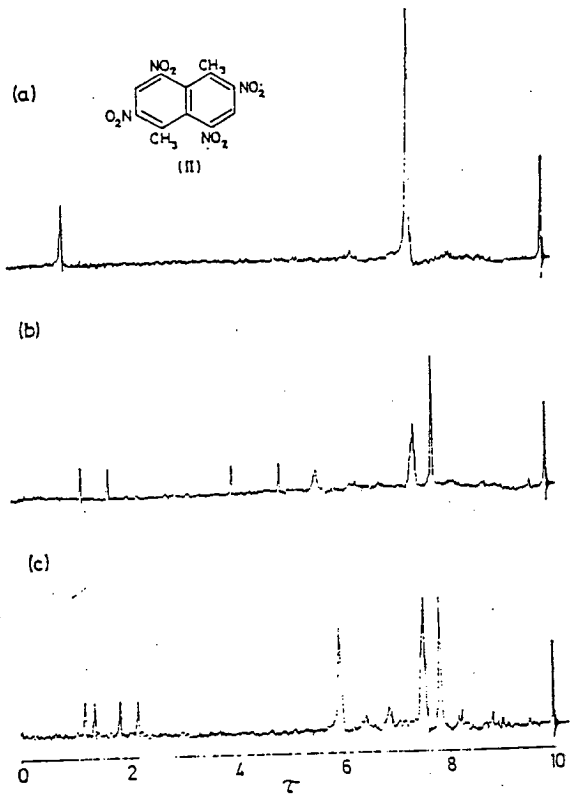


FIGURE 2 ^{1}H N.m.r. spectra of 1,5-dimethyl-2,4,6,8-tetranitronaphthalene in [$^2H_3$]dimethyl sulphoxide containing sodium [$^2H_3$]methoxide; mole ratio [CD_3O^-] : [nitroaromatic] is (a) 0.0, (b) 1.0, spectrum after 2 min, (c) 1.0, spectrum after 30 min

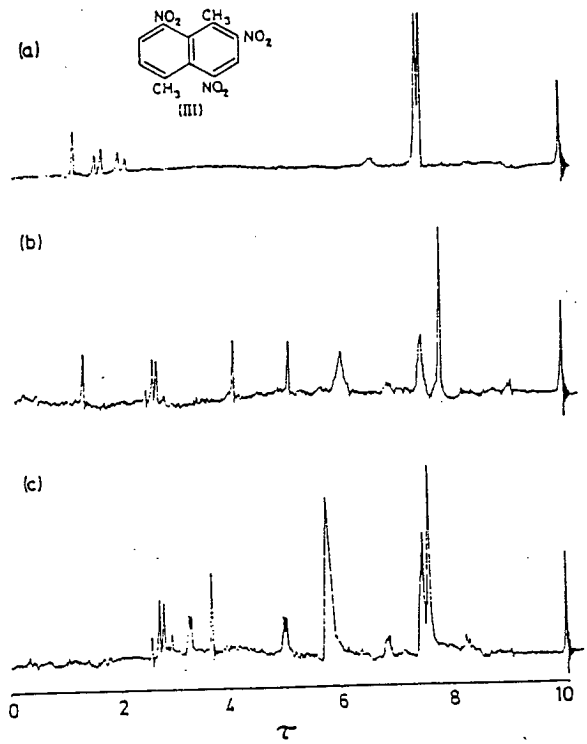


FIGURE 3 ^{1}H N.m.r. spectra of 1,5-dimethyl-2,4,8-trinitronaphthalene in [$^2H_3$]dimethyl sulphoxide containing sodium [$^2H_3$]methoxide; mole ratio [CD_3O^-] : [nitroaromatic] is (a) 0.0, (b) 1.0, and (c) 3.0

group resonances of (III). Since proton abstraction is more likely to occur from the methyl group at the 1-position in (III), the anion would be expected to have structure (X). Deuteriation of (X) in deuteriochloric acid–heavy water yielded 1,5-dimethyl-2,4,8-trinitro-[^{2}H]naphthalene.

The spectrum of Figure 3(b) does not change with time, but further addition of sodium deuteriomethoxide results in the spectrum of Figure 3(c). The resonances in the latter spectrum may be assigned on the basis of addition of methoxide at C-3 in (X) to give the adduct (XI). As would be expected, addition at C-3 causes the resonance for the proton at this site to shift upfield; from τ 1.25 to 3.68 in this case. Interestingly, coupling between the exocyclic olefinic protons is observed when conjugation between the olefinic linkage and the C-2–C-3 bond is broken by σ addition at C-3.

EXPERIMENTAL

The nitroaromatic compounds were prepared and purified as previously described.[1] [^{2}H$_6$]Dimethyl sulphoxide and [^{2}H$_4$] methanol were dried over molecular sieve.

^{1}H N.m.r. spectra were recorded at 31° on a Perkin-Elmer R10 spectrometer operating at 60 MHz. Chemical shifts were measured relative to internal tetramethylsilane as reference. Solutions were prepared immediately prior to use, and the initial n.m.r. spectra recorded within 2—4 min after preparation. Deuteriated products were prepared by drowning out samples, after recording their n.m.r. spectra, in deuteriochloric acid–heavy water mixtures. The precipitated product was filtered off, dried *in vacuo*, and the mass spectrum of the product recorded using an A.E.I. MS9 spectrometer.

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Positive and Negative Ion Mass Spectra of Nitro- and Polynitro-1,5- and -2,3-Dimethylnaphthalenes

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Robert B. Turner and **John F. J. Todd,** University Chemical Laboratory, University of Kent at Canterbury, Kent CT2 7NH

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The positive and negative ion 70 eV mass spectra of four nitro-1,5- and twelve nitro-2,3-dimethylnaphthalenes are reported. The major molecular ion fragmentations in both modes are elimination of $NO_2^{\bullet}$, $OH^{\bullet}$, and $NO^{\bullet}$. These fragmentation pathways are supported by metastable ion evidence in many instances and can be rationalised in terms of neighbouring group interactions and the stabilities of products formed. The elimination of the nitrite ion is a feature of negative ion fragmentation but is not observed to any extent in the positive ion mode.

THE positive ion mass spectra of simple nitroaromatic compounds are now relatively well characterised [1,2] and in recent years considerable attention has been given to the study of the negative ion spectra of such compounds. Included in this latter work are reports on the negative ion spectra of nitroacenaphthenes,[3] dinitrobenzenes,[4] nitrophthalic anhydrides,[5] *N*-substituted nitroanilines,[6] trinitromethanes,[7] substituted nitroarylbenzoates,[8] and

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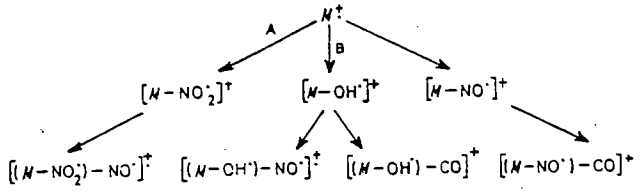
aryl nitrobenzoates.[8] In the case of negative ion spectra, molecular anions are sometimes formed which do not possess enough internal energy to enable fragmentation to occur [5] and there are also certain functional groups which under normal conditions do not fragment.[9-11] These effects, taken along with the early observations that only small numbers of negative ions are produced upon electron impact and the frequent occurrence of ions produced by ion–molecule reactions, partly account for the fact that negative ion mass spectrometry has been rarely used in conjunction with positive ion mass spectrometry to study mass spectral fragmentation. We now report on both the positive ion and negative ion mass spectra of a series of nitro- and polynitro-1,5- and -2,3-dimethylnaphthalenes and consider herein the extent to which the two types of spectra relate to each other and to the spectra of other nitroaromatic compounds.

RESULTS AND DISCUSSION

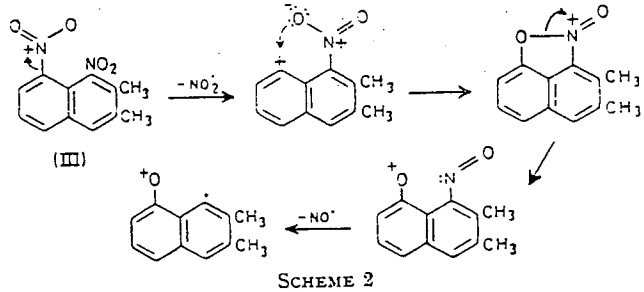
(A) *Positive Ion Mass Spectra.*—The most abundant ions in the positive ion mass spectra of the nitro-1,5- and nitro-2,3-dimethylnaphthalenes are listed in Table 1 along with the value for the percentage total ion current carried by each ion. The major fragmentation routes of the molecular ions and of the resultant daughter ions are represented in Scheme 1.



SCHEME 1

Inspection of Table 1 shows that in the case of the nitro-2,3-dimethylnaphthalenes, fragmentation route A predominates in those compounds having nitro-groups on adjacent *peri*-positions, *viz.* compounds (III), (VIII), (X), and (XII). Obviously, steric strain between nitro-groups on adjacent *peri*-positions facilitates loss of NO_2· and in each of these compounds the $[M - NO_2\cdot]^+$ ion gives rise to the base peak in the spectrum. In contrast, the degree of steric interaction between *ortho*-substituted nitro-groups is such that NO_2· loss is not favoured relative to other losses. This is seen for 5,6,8-trinitro-2,3-dimethylnaphthalene (XI) where the $[M - NO_2\cdot]^+$ ion does not give rise to a particularly prominent peak in the spectrum.

The loss of NO· subsequent to the elimination of NO_2· in those compounds having *peri*-substituted nitro-groups can occur by the mechanism shown in Scheme 2. In this Scheme, the initial loss of NO_2· leaves a positive charge at the *peri*-position which facilitates bonding to



SCHEME 2

TABLE 1

Metastable transitions [a] and percentage total ion current for important fragmentations in the positive ion mass spectra of nitrodimethylnaphthalenes

		Daughter ions											
	$M^{+\cdot}$ (%)	$[M - NO_2\cdot]^+$ m*	$[M - NO_2\cdot]^+$ %	$[M - OH\cdot]^+$ m*	$[M - OH\cdot]^+$ %	$[M - NO\cdot]^+$ m*	$[M - NO\cdot]^+$ %	$[(M - OH\cdot) - NO\cdot]^{+\cdot}$ m*	$[(M - OH\cdot) - NO\cdot]^{+\cdot}$ %	$[(M - OH\cdot) - CO]^+$ m*	$[(M - OH\cdot) - CO]^+$ %	$[(M - NO\cdot) - CO]^+$ m*	$[(M - NO\cdot) - CO]^+$ %	$[(M - NO_2\cdot) - NO\cdot]^{+\cdot}$ m*	$[(M - NO_2\cdot) - NO\cdot]^{+\cdot}$ %
Nitro-2,3-dimethylnaphthalenes															
1- (I)	14.0	*	4.2	*	2.0	*	2.0	*	2.7	*	5.7	*	1.9		
5- (II)	14.3	*	5.6		0.2		1.2	*	2.4		2.4	*	1.7		
1,8- (III)	4.8	*	14.5		0.1		0.1		0.2		1.9		0.0	*	8.8
1,5- (IV)	4.2		0.1	*	0.5		0.1		0.2		0.2		0.0		1.0
1,4- (V)	8.0		0.5	*	1.1	*	0.7		0.6	*	0.7		0.1		1.5
5,7- (VI)	7.5		1.0	*	0.4		0.1	*	0.3		0.5		0.2		1.1
5,8- (VII)	10.7		0.9	*	0.7		0.3		0.6		0.7		0.1		0.8
1,4,5- (VIII)	1.4	*	10.0		0.1		0.1		0.0		1.7		0.0	*	1.0
1,5,7- (IX)	9.8		0.2	*	3.7		0.5		0.3		0.3		0.0		0.5
1,6,8- (X)	4.0	*	14.2		0.1		0.1		0.2		2.1		0.0	*	7.1
5,6,8- (XI)	1.0		0.1	*	0.3		0.1		0.1		0.0		0.0	*	0.1
1,4,5,7- (XII)	0.1	*	2.4		0.1		0.4		0.0		0.2		0.0	* [b]	0.5
Nitro-1,5-dimethylnaphthalenes															
4- (XIII)	6.4	*	2.8	*	15.6		0.9	*	2.9	*	2.3		0.4		0.0
4,8- (XIV)	5.7		0.5	*	12.0		0.2		1.9		0.5		0.0		0.0
2,4,8- (XV)	8.3		0.1	*	6.9		0.0		0.4		0.2		0.0		0.0
2,4,6,8- (XVI)	1.7	*	0.2	*	2.0		0.0		0.4		0.2		0.0		0.0

[a] Asterisk indicates that metastable ion observed at appropriate *m/e* value. [b] Metastable ion also observed for $[(M - NO\cdot) - NO_2\cdot]^+$.

[9] J. H. Bowie, *Org. Mass Spectrometry*, 1971, **5**, 945.
[10] R. G. Alexander, D. B. Bigley, and J. F. J. Todd, *Org. Mass Spectrometry*, 1973, **7**, 643.
[11] J. H. Bowie, *Org. Mass Spectrometry*, 1974, **9**, 304.

an oxygen atom on the adjacent nitro-group. It is not possible for this mechanism to occur for the other nitro-2,3-dimethylnaphthalenes, or for the nitro-1,5-dimethylnaphthalenes, and the percentage total ion current carried by the $[(M - NO_2\cdot) - NO\cdot]^{+\cdot}$ ions formed from these compounds is correspondingly low.

The importance of steric interaction in enhancing a particular fragmentation route is also observed in situations where a methyl and a nitro-group are sited at adjacent *peri*-positions. Each of the nitro-1,5-dimethylnaphthalenes has this structural feature and in each of the spectra, except that of 2,4,8-trinitro-1,5-dimethylnaphthalene (XV), the base peak arises from the $[M - OH\cdot]^+$ ion which undoubtedly will be formed as a result of bonding between a hydrogen atom of the methyl group and an oxygen atom of the adjacent nitro-group.[12] The peak resulting from the $[M - OH\cdot]^+$ ion in the naphthalene (XIV) (14.4%) with the corresponding sum for the ions formed from 1-nitro- (I) (9.4%) and 1,4-dinitro-2,3-dimethylnaphthalene (V) (1.4%).

For compounds which do not have a nitro-group adjacent to an alkyl group the elimination of OH· will involve bonding of oxygen to a neighbouring ring hydrogen atom. Earlier reports on the loss of OH· from alkyl substituted nitroaromatic compounds[12-15] would suggest that in the case of the 5- and 8-substituted nitro-2,3-dimethylnaphthalenes bonding will occur preferentially to hydrogen in the ring not containing the nitro-group, *i.e.* at the adjacent *peri*-hydrogen atom. It is interesting to note that for the 5- and 8-substituted nitro-2,3-dimethylnaphthalenes which have an unsubstituted adjacent *peri*-position there is no loss of CO from the molecular ion, unlike the case for structurally similar nitronaphthalenes.[14,16] The key step in the elimination

TABLE 2

Metastable transitions [a] and percentage total current for important fragmentations in the negative ion mass spectra of nitrodimethylnaphthalenes

		Daughter ions																	
		$[M - NO_2\cdot]^-$		$[M - OH\cdot]^-$		$[M - NO\cdot]^-$		$[M - CH_3\cdot]^-$		$[M - HONO]^{-\cdot}$		$[(M - OH\cdot) - CO]^-$		$[(M - NO\cdot) - NO\cdot]^{-\cdot}$		$[(M - NO_2\cdot) - NO\cdot]^{-\cdot}$		NO_2^-	
	$M^{-\cdot}$ (%)	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%	m*	%
Nitro-2,3-dimethylnaphthalenes																			
1- (I)	20.6		0.8		2.0		10.9		0.0	* b,c	0.7	*	1.4						46.8
5- (II)	50.6		0.1		0.5		3.4		0.0		0.1		0.2						30.7
1,8- (III)	13.1	*	9.1		0.1		1.0		0.0		0.1		1.4		0.1	*	4.8		60.3
1,5- (IV)	32.8		0.6	*	0.9	*	8.5		0.0	* b,c	0.2		0.2	*	1.1		0.2		45.0
1,4- (V)	21.0		1.4	*	2.0	*	17.8		0.0	* b,d	0.1	*	0.4		0.4		0.2		43.0
5,7- (VI)	23.8		0.4		0.1	*	16.5		0.0		0.0		0.1	*	1.8		0.5		47.7
5,8- (VII)	48.7		1.0		0.1	*	19.5		0.0		0.1		0.5		0.2		0.4		14.6
1,4,5- (VIII)	1.4	*	9.4		0.2		2.4		0.0		0.2		1.7		0.5	*	1.0		45.1
1,5,7- (IX)	18.4	*	3.2	*	2.2	*	30.6		0.0	* b,c	1.9		0.8	*	3.6	*	2.9		9.6
1,6,8- (X)	3.6	*	9.4		0.0		1.5		0.0		0.2		1.9		0.5	*	8.5		50.9
5,6,8- (XI)	5.3	*	9.0		0.0	*	16.9		0.0		0.2		1.6		0.1	* e	5.1		14.6
1,4,5,7- (XII)	0.1	*	14.3		0.0		1.7		0.0		0.1		2.0		0.2	* e	26.5		14.3
Nitro-1,5-dimethylnaphthalenes																			
4- (XIII)	18.3		0.8		0.3	*	3.2		0.2		0.1		0.4						70.0
4,8- (XIV)	30.9	*	0.6	*	0.2	*	14.7	*	2.7	* c	1.0	*	0.3	*	1.0	*	0.2		32.3
2,4,8- (XV)	3.9	*	3.8	*	3.0	*	9.6	*	6.0	* b,d	1.6	*	2.5	*	0.9		0.4		21.0
2,4,6,8- (XVI)	1.5	*	2.1	*	2.6		2.6	*	1.9	* b,d	0.7	*	1.7		0.4		0.3		15.0

[a] Asterisk indicates that metastable ion observed at appropriate *m/e* value. [b] Corresponding to $[(M - OH\cdot) - NO\cdot]^{-\cdot}$. [c] Corresponding to $[M - HONO]^{-\cdot}$. [d] Corresponding to $[(M - OH\cdot) - NO\cdot]^{-\cdot}$. [e] Metastable ion also observed for $[(M - NO\cdot) - NO_2\cdot]^{-\cdot}$.

spectrum of compound (XV) has a relative intensity 85% that of the base peak which, in this particular case, corresponds to the molecular ion.

The likelihood of loss of OH· through interaction between neighbouring methyl and nitro-groups will be dependent upon the relative orientations of the hydrogen and oxygen atoms involved in the bonding. For the nitro-1,5- and -2,3-dimethylnaphthalenes, the relative orientations in *peri*-substituted methyl and nitro-groups are such that the loss of OH· is more favoured than the cases where these groups are *ortho*-substituted. This is highlighted by a comparison of the sum of the percentage total ion currents carried by the principal ions formed *via* route B from the fragmentation of 4-nitro- (XIII) (20.8%) and 4,8-dinitro-1,5-dimethyl-

of CO from the molecular ion of the nitronaphthalenes is bonding of an oxygen atom of the nitro-group to the carbon atom at the adjacent *peri*-position.[14] In the case of the 5- and 8-substituted nitro-2,3-dimethylnaphthalenes this step would be in competition with bonding to the hydrogen atom at the adjacent *peri*-position and this latter bonding is favoured presumably because of the effect of the electron-donating methyl groups at the 2- and 3-positions.

The values for the percentage total ion current carried by the $[M - NO\cdot]^+$ ions do not reveal that any significant structural factors control the loss of NO· from the molecular ions. This fragmentation process, which involves the nitro ⟶ nitrito rearrangement,[17] does not therefore warrant further comment at this point, although the loss of NO· from nitroaromatic compounds has previously been studied in detail.[18]

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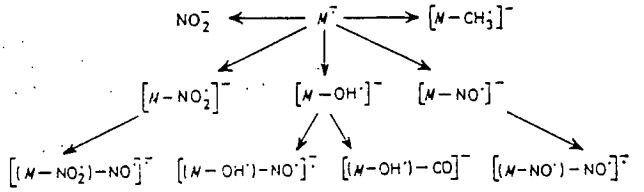
[17] J. H. Benyon, R. A. Saunders, and A. E. Williams, *Ind. chim. belge*, 1964, 311.
[18] J. H. Benyon, M. Bertrand, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1973, **95**, 1739.

(B) *Negative Ion Mass Spectra.*—The most abundant ions in the negative-ion mass spectra of the nitro-1,5- and nitro-2,3-dimethylnaphthalenes are given in Table 2 along with the value for the percentage total ion current carried by each ion. The most prominent routes for fragmentation of the molecular ions involve formation of NO_2^- or loss of $NO_2^{\bullet}$, $OH^{\bullet}$, $NO^{\bullet}$, and, in the case of the nitro-1,5-dimethylnaphthalenes, loss of $CH_3^{\bullet}$. These primary fragmentations and the major subsequent fragmentations are summarised in Scheme 3.



SCHEME 3

The results given in Table 2 show that elimination of $NO_2^{\bullet}$ from the molecular ion is enhanced for compounds in which there is steric interaction between nitro-groups, regardless of whether the interaction be between *peri*- or *ortho*-substituted nitro groups. In such compounds the loss of $NO_2^{\bullet}$ from the molecular ion predominates over loss of OH· and the peaks in their spectra corresponding to the $[M - OH^{\bullet}]^-$ ion are relatively minor. The peak arising from the $[M - OH^{\bullet}]^-$ ion is also relatively minor for those compounds which do not have a nitro-group adjacent to a methyl group. It is only for those compounds in which there is no steric interaction between nitro-groups and in which a nitro-group is adjacent to a methyl group that the peak arising from the $[M - OH^{\bullet}]^-$ ion is of some significance. The mechanism for loss of OH· *via* interaction of a nitro-group with a neighbouring alkyl group would be expected to be analogous to that for the loss of OH· from the molecular ion of 3-nitro- and 3,8-dinitro-acenaphthene.[3] The metastable ion evidence (Table 2) shows that the OH· group can be lost from the molecular ion either as an individual entity or as part of the HONO species.

The elimination of NO·, like that of OH·, plays a secondary role in the fragmentation of the molecular anions from compounds in which there is steric interaction between *peri*-substituted groups. Nevertheless, loss of NO· from the molecular anion is an important fragmentation process in the other compounds. The elimination of NO· from the molecular anion of polynitroaromatic compounds is facilitated when there is a nitro-group effectively *ortho*/*para* to the nitro-group from which the loss occurs; this being a consequence of the remaining nitro-group participating in the resonance stabilisation of the phenoxide ion formed as a result of NO· loss.[3,6] For the compounds under study, this phenomenon could only be examined for 5,7-dinitro- (VI) and 5,8-dinitro-2,3-dimethylnaphthalene (VII) in which, unlike the other compounds investigated, there is no steric interaction between *ortho*- or *peri*-substituted groups. The results given in Table 2 are in agreement with the previous findings to the extent that the $[M - NO^{\bullet}]^-$ ion from the *para*-substituted compound (VII) carries a greater percentage total ion current, *viz.* 19.5%, than the $[M - NO^{\bullet}]^-$ ion from the *meta*-substituted compound (VI), *viz.* 16.5%.

The percentage total ion current carried by the $[M - NO^{\bullet}]^-$ ion from 1,5,7-trinitro-2,3-dimethylnaphthalene (IX) is significantly higher (30.6%) than those of all the other $[M - NO^{\bullet}]^-$ ions, and, for this particular compound the $[M - NO^{\bullet}]^-$ ion gives rise to the base peak in the spectrum. Compound (IX) has the distinguishing structural feature as compared to the other compounds in that whichever of the three nitro-groups the loss of NO· occurs from, there is always a nitro-group remaining which is effectively *ortho*/*para* to the site of NO· loss and which, therefore, can stabilise the resulting phenoxide type ion.

A peak corresponding to the $[M - CH_3^{\bullet}]^-$ ion is present in the negative ion spectra of the nitro-1,5- but not in the spectra of the nitro-2,3-dimethylnaphthalenes. Previous workers have also reported that certain functional groups show no fragmentation or are not eliminated in negative-ion mass spectrometry,[11] except under conditions of collision-induced decomposition.[19] If, as has been suggested for nitroacenaphthenes,[3] the molecular anions of the nitro-1,5- and -2,3-dimethylnaphthalenes are formed by secondary electron capture, then the differences in behaviour of the molecular ions may result from differences in unpaired spin density distribution between the two sets of compounds. Hückel MO calculations show that for the radical anions of the nitro-1,5-dimethylnaphthalenes, the spin densities at the nuclear sites substituted by a methyl group are higher than the corresponding spin densities for the radical anions of the nitro-2,3-dimethylnaphthalenes. For example, the spin densities at the 1- and 5-positions in the radical anion of 4-nitro-1,5-dimethylnaphthalene (XIII) are calculated to be 0.139 and 0.157 respectively, whereas the corresponding values at the 2- and 3-positions in the radical anion of 1-nitro-2,3-dimethylnaphthalene (I) are only 0.040 and 0.057 respectively. These results indicate that electron capture has the greater effect on the C–methyl bonds in the nitro-1,5- as compared to the nitro-2,3-dimethylnaphthalenes, and that the cleavage of the C–methyl bond consequent upon electron capture might be expected to occur more readily in the nitro-1,5-dimethylnaphthalenes.

Nitrite ion formation is a major feature of the negative ion spectra. However, there is no obvious correlation between the percentage total ion current carried by this ion and the structure of the parent compound, possibly because the ion originates from a variety of fragment ions.

(C) *Comparison of Spectra.*—The positive and negative ion spectra are similar in that the principal primary fragmentations in both cases involve loss of $NO_2^{\bullet}$, $OH^{\bullet}$, and $NO^{\bullet}$. Also, the fragmentations involving loss of $NO_2^{\bullet}$ and OH· show fairly clear parallels in their behaviour for

[19] J. H. Bowie, *J. Amer. Chem. Soc.*, 1973, 95, 5795.

both sets of ions, *viz.* steric interaction facilitates elimination of the NO_2· species from both types of molecular ion, and the elimination of the OH· species from the molecular ions only occurs to a significant extent in both modes when there is an alkyl and nitro-group on adjacent sites. On the other hand, the tendency to lose NO· is different in the two sets of spectra with this ion being principally expelled in negative ion fragmentations. This may be linked to the fact that the negatively charged molecular ions tend to be more stable than the positively charged molecular ions, especially for the less highly substituted nitro-compounds, and that the molecular ions have to undergo the nitro ⟶ nitrito rearrangement prior to loss of NO·. The major difference between the two sets of spectra is the formation of the nitrite ion in the negative ion but not the positive ion mode.

The results reported herein, taken in conjunction with a previous report on the mass spectra of dinitronaphthalenes,[16] indicate that positive ion and negative ion spectra can be used as an aid in assigning substitution patterns in isomeric polynitronaphthalenic compounds. Thus for a set of isomers, those for which the $[M - NO_2\cdot]$ ion gives rise to either the base peak or a very intense peak in the spectrum are more than likely to possess *peri*-substituted nitro-groups as part of the substitution pattern.

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EXPERIMENTAL

The synthesis and purification of the compounds studied has been described elsewhere.[20,21] The mass spectra were recorded on AEI MS9 and MS902 instruments operating at source pressures of *ca.* 10^{-6} Torr and temperatures of 150—220°. Assignments of the negative ion peaks was assisted by the use of an AEI Massmaster modified for use with negative ion mass spectra.[22]

We thank the Ministry of Defence for financial support and for a grant to one of us (B. C. W.).

[5/2088 *Received*, 27*th October*, 1975]

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Photodimerisation of some systemic pyrimidine fungicides

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Agricultural chemicals when exposed to ultraviolet-visible radiation in the environment may undergo photochemical reactions which reduce their active lifetime and which may give rise to a variety of products. It is of importance, therefore, that the nature of any such reactions be understood. 5-*n*-Butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine (I) and 5-*n*-butyl-2-ethylamino-4-hydroxy-6-methylpyrimidine (II) have been developed as fungicides for the control of powdery mildew on cucurbits and cereals respectively,[1,2] and the authors have investigated the photo-reactions of these pyrimidine-based fungicides and also of the structurally related pyrimidine, 2-dimethylamino-4-hydroxy-5,6-dimeth pyrimidine (III).

When a nitrogen flushed solution of compound (I) acetonitrile was photolysed using radiation from a mediu pressure Hg lamp in the range 300–320nm, the longe wavelength absorption band of (I) ($\lambda_{max.}$ 302nm) disappear with time. Separation of the product mixture by thick lay chromatography on silica gel using chloroform – methan (95:5) as eluant gave four products (R_f 0·32 (A), 0·28 (B 0·23 (C), 0·17 (D)). Field desorption mass spectra of th products exhibited a molecular ion peak at *m/e* 418 and a

intense peak at *m/e* 209 showing that the products were dimers of compound (I). As might be expected for dimeric products, the electron impact mass spectra did not give an observable molecular ion peak and were closely similar to that of (I). The ultraviolet absorption spectra of the products showed only end-absorption at 220nm and a gradual tailing to 300nm suggesting that dimerisation had been accompanied by loss of conjugation in the parent pyrimidine. This, taken in conjunction with the fact that four dimers are formed, can be explained by dimerisation across the 5,6-bond of compound (I) to give the cyclobutane derivatives (IV)–(VII). As expected for cyclobutanes of this type,[3] photolysis of solutions of (IV)–(VII) in acetonitrile with 254nm radiation resulted in dissociation of the dimers. This was shown by the reappearance on photolysis of the absorption band at 302nm corresponding to compound (I).

The same results were obtained for the four products isolated from the photolysis of (II) and (III) in acetonitrile, except that field desorption mass spectra were not recorded. It may be concluded, however, that the products from (II) and (III) would have analogous structures to those from (I).

Product mixtures from the photolysis of 2-^{14}C labelled (I) in benzene, acetone and acetonitrile were separated by t.l.c. chromatography and the photo-dimers A, B, C and D quantitatively analysed by liquid scintillation counting. The relative yield of each dimer, expressed as a percentage of the total dimer yield, is given in the Table along with the corresponding values for the four cyclobutane-type dimers derived from photolysis of 1,3-dimethyluracil.[4] The photo dimers from 1,3-dimethyluracil are labelled A, B, C and D in the Table in order of decreasing R_f as are the photodimers from (I).

Table **Variation of dimer yield with solvent**

Solvent	Pyrimidine	Yield of dimer as a percentage of total dimer yield A	B	C	D
Benzene	(I)	24	17	39	20
	1,3-dimethyluracil[4]	22	15	40	23
Acetone	(I)	15	20	16	49
	1,3-dimethyluracil[4]	11	24	16	49
Acetonitrile	(I)	13	31	20	36
	1,3-dimethyluracil[4]	8	30	27	35

The stereochemistry of the photo-dimers from 1,3-dimethyl uracil has been established,[5] and from the similarity betwee the relative yields of the photo-dimers from 1,3-dimethyl uracil and from (I) in the different solvents, it is likely tha corresponding A, B, C and D dimers have the same stereo structure. If so, the structural assignments for the photodimer from (I) would be : A = *trans-anti* (IV), B = *trans-syn* (V C = *cis-anti* (VI), D = *cis-syn* (VII).

Dimers have not been detected in crops, soils or wate which were treated with (I) and (II) and exposed to sunligh under natural conditions.

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Kinetic and Energetic Aspects of the Photodimerisation of Some Systemic Pyrimidine Fungicides

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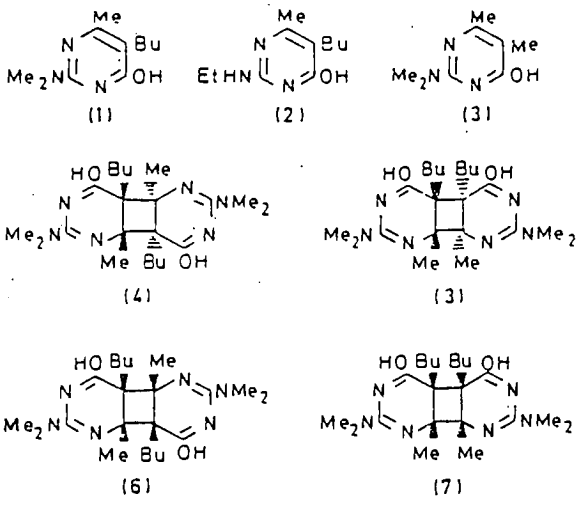
The photodimerisation of 2-dimethylamino-4-hydroxy-6-methyl-5-n-butyl- (1), 2-ethylamino-4-hydroxy-6-methyl-5-n-butyl- (2), and 4-hydroxy-5,6-dimethyl-2-dimethylamino-pyrimidine (3) has been investigated in acetonitrile. Quenching experiments have shown that the formation of photodimers involves a triplet state of (1)—(3), the energies of which have been estimated. The quantum yields for intersystem crossing from the singlet to triplet manifolds of (1)—(3) fall in the range 0.09—0.11, and the quantum yields for photodimerisation fall in the range 0.07—0.08. Rate constants for radiationless decay of the triplet state pyrimidines have been determined ($2.1—3.0 \times 10^5\ s^{-1}$), and also the rate constants for reaction of the triplet states of (1)—(3) with the corresponding ground state pyrimidine ($1.5—2.0 \times 10^8\ l\ mol^{-1}\ s^{-1}$). The efficiency of the triplet state dimerisation reactions of (1)—(3) is high compared with that of the analogous triplet state reactions of the biologically important pyrimidines, thymine and uracil.

EXPOSURE of agricultural chemicals to u.v.–visible radiation may reduce their active lifetime and may give rise to a variety of products. Consequently it is important to have an understanding of the mechanism whereby such chemicals undergo photochemical reaction so that, if necessary, the reactions can be prevented or modified.

2-Dimethylamino-4-hydroxy-6-methyl-5-n-butyl- (1) and 2-ethylamino-4-hydroxy-6-methyl-5-n-butyl-pyr-

imidine (2) are used as systemic fungicides for the control of powdery mildew on cucurbits and cereals repectively,[1,2] and we report herein on the mechanism of the photoreactions of (1) and (2) in acetonitrile, and of



the structurally related compound 4-hydroxy-5,6-dimethyl-2-dimethylaminopyrimidine (3), in the same solvent. The products from each of these photoreactions have been characterised previously [3] as stereoisomers formed by dimerisation across the 5,6-bond of the parent pyrimidine; the structures of the products from (1) being (4)—(7).

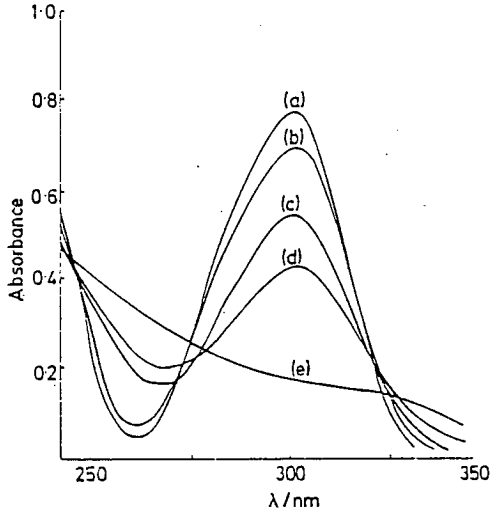


FIGURE 1 Absorption spectrum of a 4.0×10^{-4}M degassed solution of (1) in acetonitrile after photolysis for (a) 0, (b) 6, (c) 15, (d) 20, and (e) 30 h

RESULTS AND DISCUSSION

Photolysis of (1)—(3) in degassed acetonitrile solutions with Hg radiation in the range 290—330 nm brings about photochemical reaction as indicated by the disappearance with time of the longest wavelength absorption band of the substrate. A typical set of absorption spectra recorded after different photolysis times are shown in Figure 1. Monitoring the disappearance of the substrates with time gave plots which showed that the reactions followed first-order kinetics. A plot for (1) is shown in Figure 2(a); similar plots were obtained for (2) and (3).

The effect of added *cis*-penta-1,3-diene on the photoreaction of (1) is also shown in Figure 2, where it can be seen that the added diene virtually completely quenches the reaction. The same effect was observed for the photolysis of (2) and (3) in the presence of *cis*-penta-1,3-diene. G.l.c. analysis of the reaction mixtures revealed that *trans*-penta-1,3-diene had been formed as a result of the photolysis. Since *cis*-penta-1,3-diene does not absorb

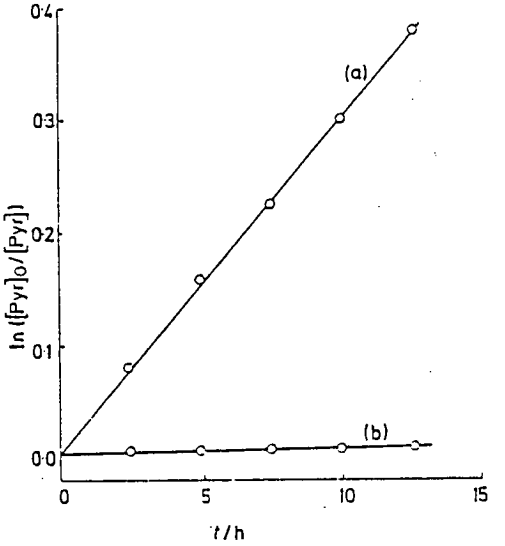


FIGURE 2 First-order kinetic plots for photolysis of a 5.0×10^{-4}M degassed solution of (1) in acetonitrile in (a) the absence of *cis*-penta-1,3-diene and (b) the presence of *cis*-penta-1,3-diene (1.0×10^{-2}M)

at the wavelengths used for irradiation it is apparent that energy transfer from the pyrimidines had brought about the *cis–trans* isomerisation of penta-1,3-diene. As the energy of the lowest excited singlet state of *cis*-penta-1,3-diene is 544 kJ mol^{-1}, considerably higher than that of the pyrimidines under study (*ca.* 370 kJ mol^{-1}), singlet–singlet energy transfer is an unlikely mechanism for quenching of the photodimerisation of (1)—(3). Since the *cis–trans* isomerisation of penta-1,3-diene can proceed *via* a triplet state diene species,[4] it can be concluded that the quenching of photodimerisation occurs by triplet energy transfer to the diene.

Prolonged irradiation of (1)—(3) in the presence of either *cis*- or *trans*-penta-1,3-diene leads to the establishment of a photostationary state, as shown for (1) in Figure 3. The *trans* : *cis* ratio at the photostationary

[1] R. M. Bebbington, D. H. Brooks, M. J. Geoghegan, and B. K. Snell, *Chem. and Ind.*, 1969, 1512.
[2] R. S. Elias, M. C. Sheppard, B. K. Snell, and J. Stubbs, *Nature*, 1968, 219, 1160.
[3] B. D. Cavell, S. J. Pollard, and C. H. J. Wells, *Chem. and Ind.*, 1976, 566
[4] G. S. Hammond, J. Saltick, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, 86, 3197.

state being close to 2.1 : 1 in each case enables the energy of the lowest triplet state of (1)—(3) to be estimated from the results of Hammond *et al.*[4] as either *ca.* 230 or 270 kJ mol^{-1}. The latter value may be compared with values in the range 291—305 kJ mol^{-1} obtained from the phosphorescence spectra of (1)—(3).[5] Since the method of Hammond *et al.* for deriving triplet state energies invariably gives low values for unsaturated compounds, the value of 270 kJ mol^{-1} is as expected in relation to that obtained from phosphorescence measurements.

As the energies of the lowest triplet state of *cis*- (238) and *trans*-penta-1,3-diene (246 kJ mol^{-1}) are lower than that of the lowest triplet state of (1)—(3), the most probable mechanism for quenching of the photodimerisation

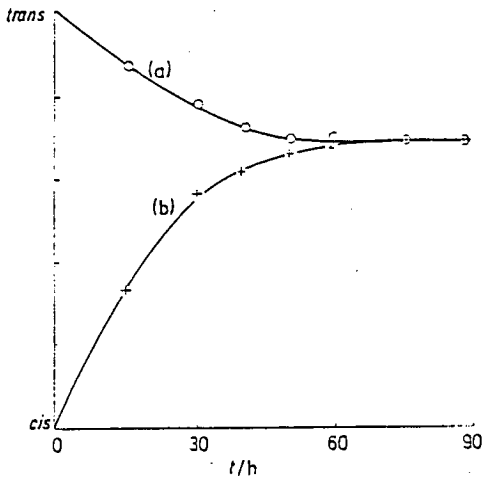


FIGURE 3 Photolytic *cis–trans* isomerisation of penta-1,3-diene in a 4.8 × 10^{-4}M solution of (1) in degassed acetonitrile containing initially (a) 100% *trans*-penta-1,3-diene (1.0 × 10^{-3}M) and (b) 100% *cis*-penta-1,3-diene (1.0 × 10^{-3}M). Composition at photostationary state is 67.7% *trans*- and 32.3% *cis*-penta-1,3-diene

of (1)—(3) is by direct triplet–triplet energy transfer. Furthermore, since the quenching was, to all extents and purposes, 100% efficient it is apparent that, at the concentrations used, the photodimerisation of (1)—(3) proceeds virtually entirely by way of triplet state pyrimidine. It is to be noted that for such a situation, the kinetics of addition of triplet state to ground state pyrimidine to form a dimeric species would be first order with respect to the pyrimidine.

The quantum yield for formation of triplet state pyrimidine is equal to the quantum yield, Φ_{isc}, for intersystem crossing from the singlet to triplet state manifold, and was determined for each pyrimidine by using the photosensitised *cis–trans* isomerisation of penta-1,3-diene as a means of counting the triplet states formed on irradiation.[6] The values so determined for Φ_{isc} are given in the table. In a similar fashion, irradiation of solutions of the pyrimidines both in the absence and presence of added *cis*-penta-1,3-diene, followed by product analysis, allowed measurement of the ratio of the quantum yield of dimerisation, Φ_{dim}, to that for intersystem crossing Φ_{isc}. The values of Φ_{dim} derived from this ratio are listed in the Table.

Quantum yield and kinetic data for photodimerisation

Pyrimidine	Φ_{isc}	Φ_{dim}	$10^5 k_d/s^{-1}$	$10^8 k_r/$ l mol^{-1} s^{-1}
(1)	0.09 ± 0.01	0.07 ± 0.01	2.09 ± 0.07	1.72 ± 0.13
(2)	0.09 ± 0.01	0.06 ± 0.01	2.37 ± 0.07	1.46 ± 0.15
(3)	0.11 ± 0.01	0.08 ± 0.01	2.99 ± 0.06	2.04 ± 0.20

The quantum yield data given in the Table show that, at the pyrimidine concentrations employed, between 66 and 77% of the triplet state molecules formed react to give photodimers. This is in marked contrast to the photodimerisation of thymine (2,4-dihydroxy-5-methylpyrimidine) and uracil (2,4-dihydroxypyrimidine), two biologically important pyrimidines which play a direct role in the photodenaturation of DNA and RNA respectively.[7,8] Thus, photoexcitation of thymine and uracil under similar experimental conditions to those used in the present work gives rise to triplet states of which only 1.4% in the case of thymine and 4.9% in the case of uracil react to give photodimers.[9] The low conversion to photodimers in the case of thymine and uracil is a consequence of the formation of a metastable dimeric species (by addition of a triplet state molecule to a ground state molecule) which either stabilises to form products or reverts to ground state molecules, with the latter route predominating. If such a metastable dimeric species is formed during the reaction of the triplet state of (1)—(3) with ground state pyrimidine, then obviously this species has a higher efficiency of conversion into products and a smaller efficiency of splitting to ground state pyrimidine than is the case for thymine and uracil.

Applying the steady-state approximation method to a simple reaction mechanism in which the pyrimidine substrate is consumed *via* reaction of triplet with ground state pyrimidine gives expressions (1) and (2) where Φ_0

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \quad (1)$$

$$1/\tau = k_d + k_r[Pyr] \quad (2)$$

and Φ represent the respective quantum yields for consumption of pyrimidine in the absence and presence of quencher [Q], τ is the lifetime of the triplet state, [Pyr] is the concentration of ground-state pyrimidine, and k_q, k_d, and k_r are the respective rate constants for quenching of the triplet state, unimolecular radiationless decay of the triplet state, and reaction of triplet state with ground state pyrimidine. A Stern–Volmer plot according to equation (1) is shown for compound (1) in Figure 4; similar plots were obtained for (2) and (3). The plots were linear up to high values of Φ_0/Φ reinforcing the conclusion that, at the concentrations of pyrimidine used, the photodimerisation occurs *via* the triplet state.

In view of the difference between the triplet state energies of the pyrimidines and of the quenching agents

[5] D. Sen and C. H. J. Wells, unpublished results.

[6] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 1965, 43, 2129.

[7] J. G. Burr, *Adv. Photochem.*, 1968, 6, 193 and references cited therein.

[8] R. B. Setlow, *Photochem. and Photobiol.*, 1968, 7, 643.

[9] P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, 1970, 92, 181.

used in these studies, it may be assumed that quenching is diffusion controlled and that the rate constant, k_q, will

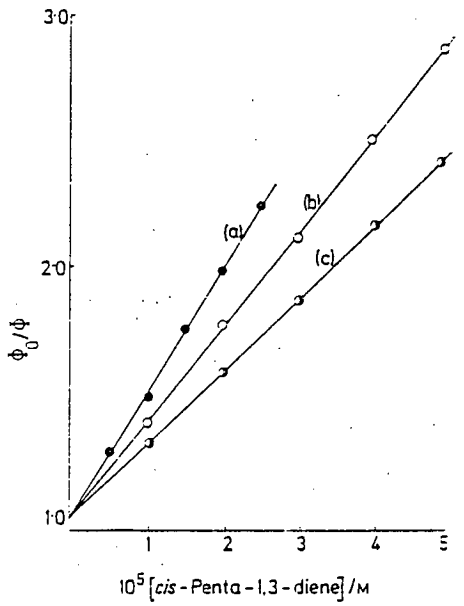


FIGURE 4 Representative Stern–Volmer plots for photolysis of degassed acetonitrile solutions of (1): (a) 1.0×10^{-4}, (b) 5.0×10^{-4}, and (c) 10.0×10^{-4}M

have the diffusion controlled value of 1.1×10^{10} l mol^{-1} s^{-1} in acetonitrile.[9] Using this value, the slopes of the Stern–Volmer plots yielded values for the triplet state lifetimes, τ, which when plotted against pyrimidine concentration according to equation (2) gave the straight line plots shown in Figure 5. The intercepts and slopes of these plots yielded the values for k_d and k_r listed in the Table.

The rate constant values for (1) were checked by monitoring the rate of formation of photodimers from 2-^{14}C labelled (1) using t.l.c. for product separation followed by liquid scintillation analysis. The build-up of photo-

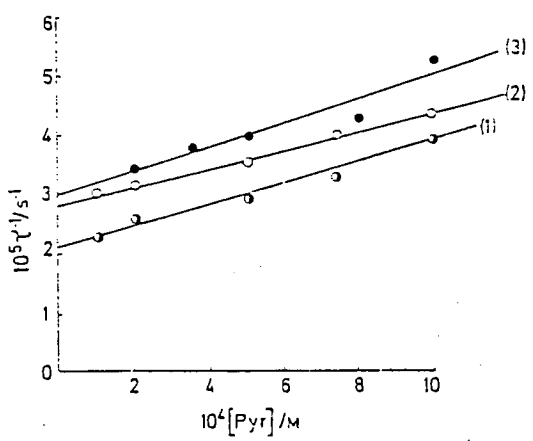


FIGURE 5 Plot of reciprocal of triplet state lifetime *versus* pyrimidine concentration

dimers with time is plotted in Figure 6 where the total dimer yield is expressed as a percentage of the initial activity. For a mechanism in which photodimers are formed by reaction of triplet state with ground state pyrimidine, the initial rate, R, of dimer formation is given by expression (3) [10] where a is a constant specific to

$$\frac{1}{R} = \frac{1}{a} + \frac{k_d}{ak_r} \cdot \frac{1}{[\text{Pyr}]} \qquad (3)$$

each pyrimidine. Since a dimer represents two pyrimidine molecules, the initial rate of dimer formation is given by one-half the initial slope of the graph of dimer

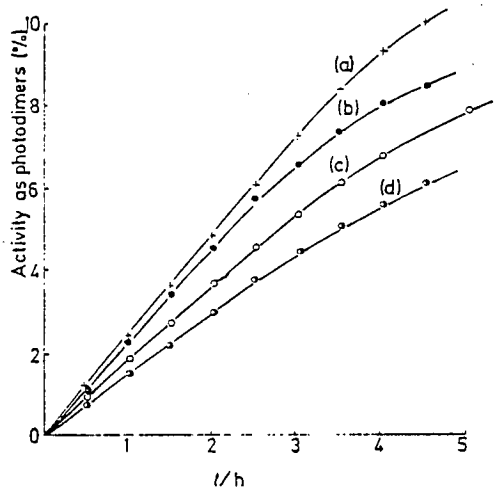


FIGURE 6 Yield of dimers from photolysis of degassed acetonitrile solutions of 2-^{14}C labelled (1): (a) 4.0×10^{-4}, (b) 5.0×10^{-4}, (c) 7.0×10^{-4}, and (d) 10.0×10^{-4}M

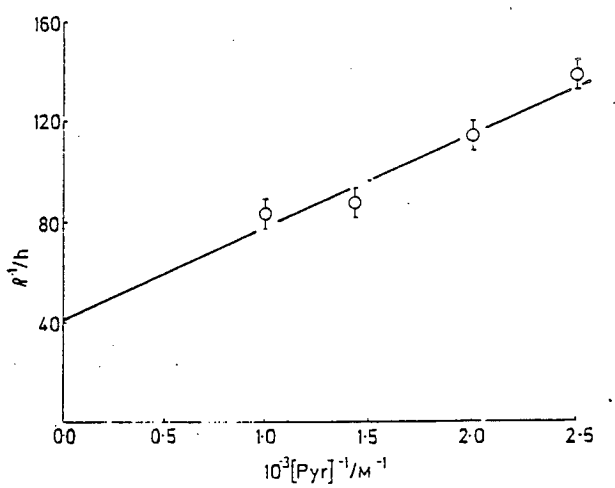


FIGURE 7 Plot of reciprocal of initial rate of dimer formation *versus* reciprical of concentration of (1)

yield *versus* time (Figure 6). A plot according to equation (3) is shown in Figure 7. The ratio k_d/k_r derived from the slope and intercept of the straight line shown in the plot is 0.9×10^{-3} mol l^{-1} which may be compared with the value of 1.2×10^{-3} mol l^{-1} derived from the values given in the Table.

The rate constants for addition of triplet state to ground state pyrimidine for (1)—(3) fall in the range

[10] I. H. Brown and H. E. Johns, *Photochem. and Photobiol.* 1968, 8, 273.

1.5—2.0 × 10^8 l mol^{-1} s^{-1} which is markedly lower than the values determined [9] for the corresponding rate constants for thymine (7.0 × 10^8 l mol^{-1} s^{-1}) and uracil (20.0 × 10^8 l mol^{-1} s^{-1}). The similarity in the rate constants for (1)—(3) is not unexpected in view of the similarity in substituents, and hence electron density, at the C(5)–C(6) bond across which dimerisation occurs. Photodimerisation in thymine and uracil also occurs across the C(5)–C(6) bond, and the change in rate constant values in the order (1) ~ (2) ~ (3) < thymine < uracil most probably reflects the decreasing steric hindrance at the C(5)–C(6) bond is going from (1)—(3) to uracil.

EXPERIMENTAL

Acetonitrile was purified by the method of O'Donnell *et al.*[11] and distilled through a 30 plate spinning band column so that there was no absorption above 260 nm. The distilled acetonitrile was stored in the dark under nitrogen and used within three weeks. The purity of *cis*- (K and K) and *trans*-penta-1,3-diene (K and K) was checked by g.l.c., only material of >99% purity being used. Compounds (1) and (2) were supplied by Plant Protection Division, I.C.I. Limited, and were recrystallised twice from methanol prior to use. Compound (3) was prepared by an adaptation of the method of Hull *et al.*[12] 1,1-Dimethylguanidine sulphate (27.2 g) was added to ethanolic sodium ethoxide, prepared by adding clean sodium (4.6 g) to redistilled absolute ethanol (150 cm^3). The mixture was shaken for 15 min, then ethyl 2-methylacetoacetate (28.8 g) was added, and the solution allowed to stand for 18 h, after which time it was refluxed for 2 h, cooled, filtered, and the filtrate evaporated to low volume whence (3) crystallised as needles. Recrystallisation from methanol yielded product (8.4 g), m.p. 169—173°.

G.l.c. analysis of *cis*- and *trans*-penta-1,3-diene were performed on an Aerograph 660 chromatograph using an 8.5 m × 3 mm column packed with 25% 1,2,3-tris-(β-cyanoethoxy)-propane on 40—60 mesh Chromosorb W. Absorption spectra were recorded on a Unicam SP 8000 spectrophotometer and quantitative analysis of (1)—(3) was carried out at 302 nm on a Unicam SP 500 spectrophotometer. T.l.c. was performed on Merck silica gel F_{254} plates (0.2 mm × 20 cm × 20 cm) using chloroform–methanol (95 : 5) as eluant. Autoradiograms were taken using Ilford *X*-ray film. Liquid scintillation was carried out on an Ekco Electronics N664A instrument connected to a Nuclear Enterprises ST3 digital counter.

Samples were prepared for photolysis by pipetting sample solution (4 cm^3) into 10 mm i.d. quartz tubes, connected by graded seal to a Pyrex socket, and degassed by a repeated freeze–thaw cycle until a vacuum of at least 0.3 N m^{-2} was achieved, and then sealed *in vacuo*. Each sample was prepared in duplicate or triplicate. Up to 28 sample solutions were simultaneously photolysed using a 500 W Hanovia medium-pressure Hg arc lamp located in a quartz well at the centre of a ' merry-go-round ' apparatus [13] which itself was located in a constant temperature bath maintained at 25°. For photolysis using radiation in the range 290—330 nm, the lamp radiation was filtered by means of a Chance OX7 glass filter (2 mm) in combination with a filter solution of potassium chromate (1.05 g in 2 dm^3 of 1% aqueous sodium carbonate) pumped through the annulus in the quartz well and through a heat exchanger. This filter combination had a transmission maximum at 313 nm and cut-offs at 290 and 330 nm.

Kinetic plots, such as shown in Figure 1, were derived from data obtained by photolysing solutions of the pyrimidines (3.5—5.0 × 10^{-4}M) in acetonitrile with solutions of the same concentration of pyrimidine but containing *cis*-penta-1,3-diene (5.0 × 10^{-3}M). Samples were withdrawn at various times and, after appropriate dilution, the absorbance of the parent pyrimidine in the solutions measured at 302 nm. The ratio of the absorbance of the solutions before photolysis to that at intervals during photolysis gave the ratio $[Pyr]_0/[Pyr]$. Values for the ratio Φ_0/Φ used in plots of the type shown in Figure 4 were derived from data obtained by photolysing for a specified time degassed solutions of the pyrimidines of fixed concentration (2—10 × 10^{-4}M) containing various concentrations of *cis*-penta-1,3-diene (1—5 × 10^{-5}M) alongside degassed solutions containing the same concentration of pyrimidine but without added *cis*-penta-1,3-diene. The ratio of the drop in absorbance at 302 nm for the unquenched solutions on photolysis to the drop in absorbance for each quenched solution gave the ratio Φ_0/Φ.

The procedure for the determination of the quantum yield, Φ_{isc}, of intersystem crossing from the singlet to triplet state manifold was as follows. Two sets of degassed acetonitrile solutions of composition (a) 5.0—7.0 × 10^{-4}M in pyrimidine and 5 × 10^{-4}M in *cis*-penta-1,3-diene, and (b) 2.0 × 10^{-2}M in benzophenone and 5.0 × 10^{-3}M in *cis*-penta-1,3-diene were simultaneously photolysed and after a suitable time the percentage conversion of *cis*- to *trans*-penta-1,3-diene in each solution was determined by g.l.c. The photolysis time was chosen such that the photostationary state at which the ratio *cis* : *trans* is constant was not reached, typical *cis–trans* conversions for the pyrimidine solutions were in the range 15—20% for a photolysis time of 10 h. The same amount of radiation was absorbed by solutions (a) and (b) at the concentrations used, and all triplet states formed would be quenched by energy transfer to the penta-1,3-diene. The ratio of the quantum yield of intersystem crossing in each of the pyrimidines to that in benzophenone was determined using the expressions of Lamola and Hammond,[6] and the Φ_{isc} values for the pyrimidines were calculated from these ratios on the basis that Φ_{isc} for benzophenone is unity.[6]

The ratio of the quantum yield, Φ_{dim}, for formation of dimers to the quantum yield for intersystem crossing in the pyrimidines was determined by simultaneous photolysis of degassed acetonitrile solutions of the pyrimidines (5.0—7.0 × 10^{-4}M) in the absence and in the presence of the quencher, *cis*-penta-1,3-diene (5.0 × 10^{-2}M). The percentage drop in the absorbance of the pyrimidines at 302 nm in the unquenched solutions gave a measure of the number of pyrimidine triplets reacting to give dimers. Also, the percentage conversion from *cis*- to *trans*-penta-1,3-diene in the totally quenched systems when divided by the factor of 0.55 to take into account the reverse conversion *trans* to *cis*,[6] gave a measure of the total number of pyrimidine triplets formed. The two sets of percentage values gave the ratio $\Phi_{dim} : \Phi_{isc}$.

Liquid scintillation data was obtained from four sets of degassed acetonitrile solutions of 2-^{14}C labelled (1) (4.0—

[11] J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Analyt. Chem.*, 1965, **37**, 1161.

[12] R. Hull, B. J. Lovell, H. T. Openshaw, L. C. Payman, and A. R. Todd, *J. Chem. Soc.*, 1946, 357.

[13] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1969, **1**, 245.

10.0×10^{-4}M) which were simultaneously photolysed in the reactor. Samples from each of the four sets were withdrawn at regular intervals, evaporated down, the residue dissolved in a small volume of methanol, and the products separated by t.l.c. The regions on the plates shown by autoradiography to contain the four photodimers were combined, and the activity residing in the combined photodimers in each sample was determined by liquid scintillation analysis.

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Student Review

Colour, structure and electrons

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Couleur, structure et électrons—un aperçu pour stagiares

Farbe, Struktur und Elektronen—Eine Studentenbesprechung

The rainbow is a dramatic display in nature of the range of colours in the visible spectrum—violet, indigo, blue, green, yellow, orange and red. This phenomenon of the dispersion of sunlight into its component colours was reported by Newton in 1672 when he observed that sunlight shining through a glass prism also gave rise to the visible spectrum. Since then the factors which give rise to colour in organic compounds have been the subject of extensive study, and the relationship between colour, structure and the electronic processes occurring in organic compounds is now well understood.

When visible radiation is absorbed by a molecular system, the energy uptake results in the promotion of an electron from a molecular orbital of lower energy to one of higher energy. It may be considered that molecular orbitals are formed by a linear combination of the atomic orbitals of atoms within the molecular structure. The combination of two atomic orbitals gives rise to two molecular orbitals—one a bonding orbital and the other an anti-bonding orbital—and the electrons forming the σ or π bond in the molecular structure occupy the corresponding bonding orbital. There is a third type of molecular orbital to be considered in the case of organic compounds containing heteroatoms. In this situation, those electrons associated with the heteroatom which are not involved in the bonding system of the molecule occupy non-bonding molecular orbitals (n-orbitals). This is illustrated for formaldehyde in Fig. 1 where there are two electrons in the non-bonding $2p_y$ orbital on the oxygen atom.

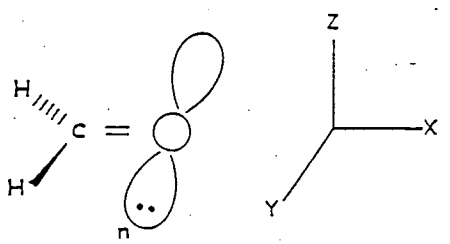


Fig. 1. Non-bonding orbital in formaldehyde

The relative energies of the different types of molecular orbital in organic molecules is shown in Fig. 2. The energy of a non-bonding orbital is normally greater than that of a σ or π orbital, but less than that of the anti-bonding orbitals. However, there are instances of molecules having a high degree of conjugation where the energy of the π orbital is greater than that of the n orbital.

The possible types of electronic transition between orbitals in organic compounds are represented by the vertical arrowed lines in Fig. 2. Electronic transitions occur upon absorption of electromagnetic radiation of energy equal to the energy difference between the orbital from which the electron originates and the orbital into which the electron is promoted,

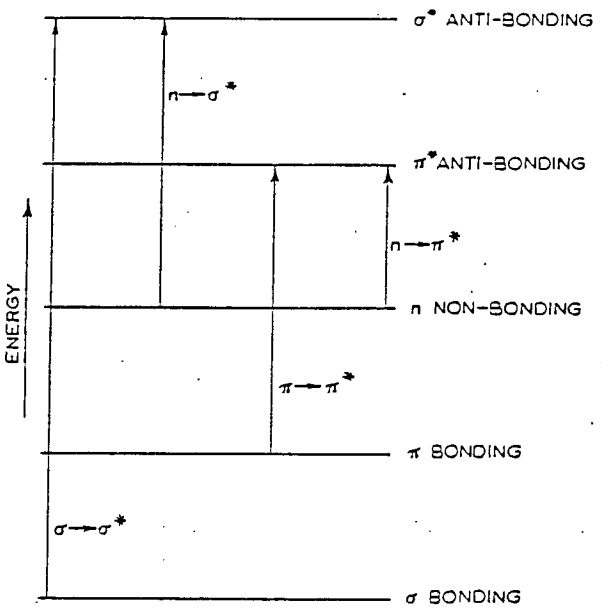


Fig. 2. Relative energies of molecular orbitals and possible transitions between orbitals

and are seen as absorption bands in the ultraviolet/visible absorption spectrum of a compound. For example, the ultraviolet absorption spectrum of formaldehyde exhibits three bands (Fig. 3) and these have been assigned to the different types of electronic transition as shown in Fig. 3. The $n \rightarrow \pi^*$ transition which gives rise to the absorption band at 280nm can be depicted in terms of the electron configuration

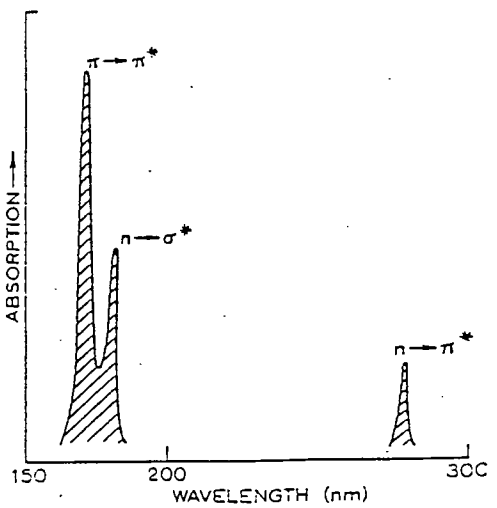


Fig. 3. Absorption spectrum of formaldehyde

of the molecule before and after the transition in the following way:

[inner electrons] $\sigma^2\pi^2n^2$ $\xrightarrow[\text{transition}]{n\rightarrow\pi^*}$ [inner electrons] $\sigma^2\pi^2n^1(\pi^*)^1$

Ground state, S_0 *Excited state, S_1*

Here, the ground state molecule S_0 is converted to an energetically excited state molecule S_1 upon absorption of the energy required to promote the $n\rightarrow\pi^*$ transition. This transition and the other two transitions, $n\rightarrow\sigma^*$ and $\pi\rightarrow\pi^*$, which give rise to the absorption bands of Fig. 3 are represented by the vertical arrowed lines in Fig. 4.

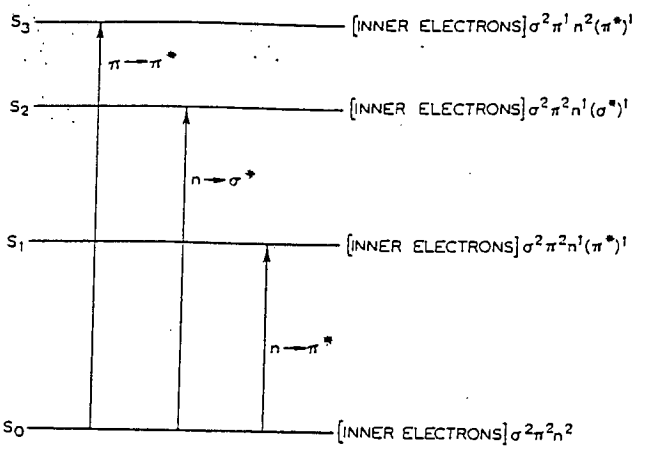
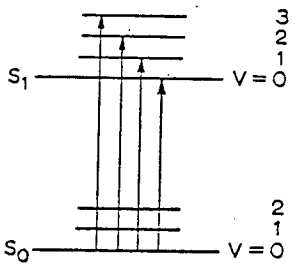


Fig. 4. Electronic states of formaldehyde and electronic transitions between states

A band in an ultraviolet/visible absorption spectrum is indicative of an electronic transition, and since the band spreads over a range of wavelengths, the corresponding electronic transition must occur over a range of energies. This is a consequence of the fact that each electronic state (S_0, S_1, S_2 . . .) has an associated set of vibrational energy levels. These levels are quantised and each has a vibrational quantum number, V. As shown in Fig. 5a, there can be a number of transitions originating from the lowest vibrational level ($V=0$) of an S_0 state to the various vibrational levels of the S_1 state, and these transitions will require slightly different energies. If a high resolution spectrometer is used to record the absorption spectrum then the individual transitions may sometimes be observed in the form of vibrational fine structure on the absorption band (Fig. 5b). Normally, however, bands in the absorption spectra of compounds in the solid state or in solution do not exhibit fine structure and only the band envelope (dotted line of Fig. 5b) is observed. Obviously, vibrational energy levels play an important role in determining the colour of a compound since the existence of these levels causes the absorption of the compound to be spread over a range of wavelengths.



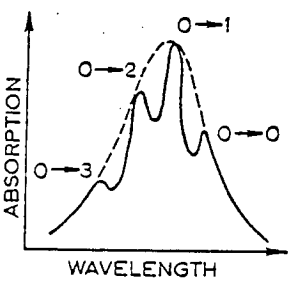


Fig. 5a. Electronic-vibrational transitions, and

Fig. 5b. Absorption band showing vibrational fine structure

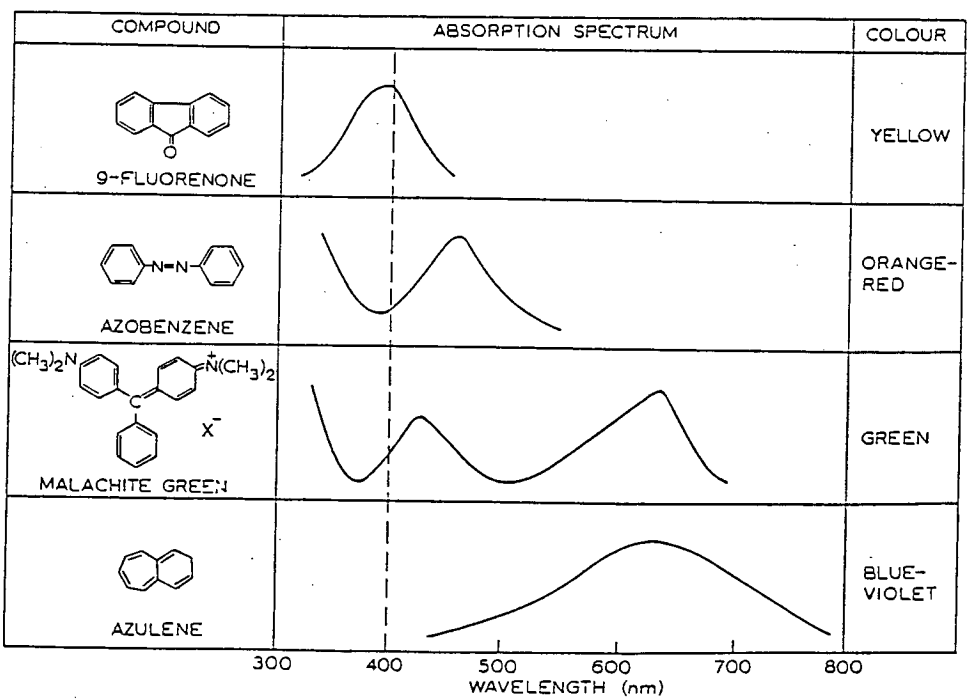


Fig. 6. Relationship between colour and absorption in the visible region

Compounds are coloured when one or more of the absorption bands fall within the wavelength range of visible radiation (Fig. 6). For organic compounds, such bands usually correspond to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions. The other possible electronic transitions, $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$, normally require greater energy than $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions, so that the corresponding absorption bands occur at shorter wavelengths, usually outside the visible region.

The energy range of the visible region is from 4.96×10^{-19} J (equivalent to 400nm) to 2.48×10^{-19} J (800nm), and for an organic compound to be coloured the energy difference between an n and a π^* orbital or between a π and a π^* orbital must fall within this range. Compounds in which this occurs generally possess one or more of the following structural features:

(i) an extended conjugated system of double bonds,

(ii) a conjugated system of multiple bonds, which involves atoms having non-bonding electrons,

(iii) a multiple bonded system, involving non-bonding electrons and charges.

The relationship between colour and the extent of double bond conjugation is demonstrated in Fig. 7 for a series of

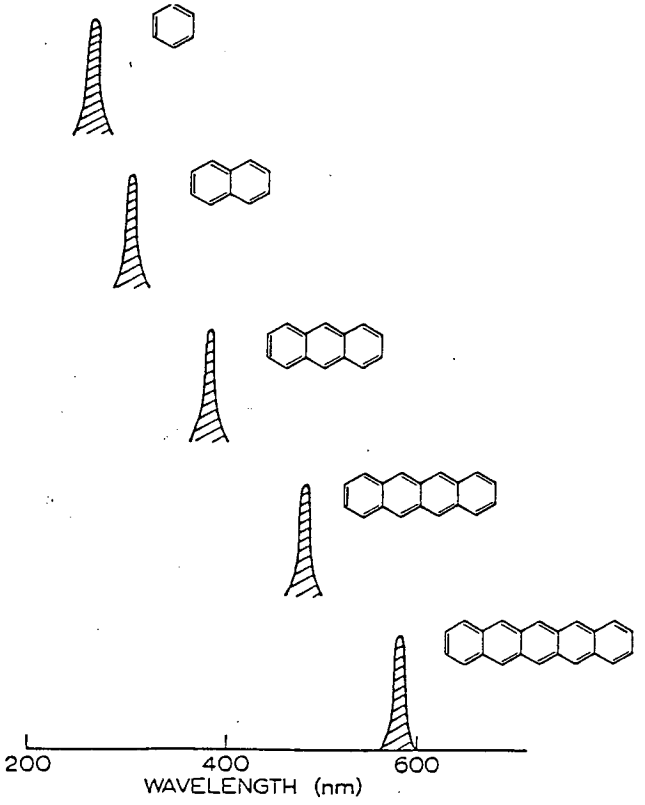
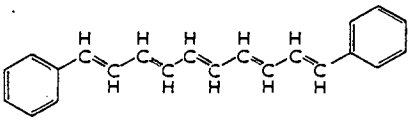
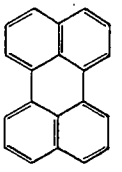


Fig. 7. Band envelope of longest wavelength absorption band of some aromatic hydrocarbons

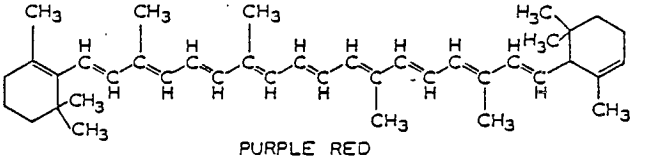
hydrocarbons—benzene, naphthalene, anthracene, naphthacene and pentacene. The Figure shows the position of the longest wavelength absorption band for each of the compounds, and it can be seen that as the extent of conjugation increases so the band moves to longer wavelengths, and that in the case of naphthacene and pentacene the band has moved into the visible region. Naphthacene and pentacene are coloured yellow and blue respectively, whilst benzene, naphthalene and anthracene are colourless. The bands in Fig. 7 each represent a $\pi \rightarrow \pi^*$ transition, and thus the effect of increasing conjugation is to decrease the energy for the $\pi \rightarrow \pi^*$ transition. Examples of other coloured compounds exhibiting extended conjugation and which have $\pi \rightarrow \pi^*$ absorption bands in the visible region are given in Fig. 8.



ORANGE



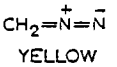
YELLOW



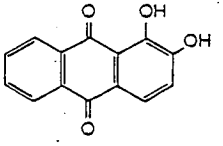
PURPLE RED

Fig. 8. Some examples of compounds which are coloured due to the influence of extended conjugation

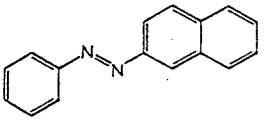
Absorption bands arising from $n \rightarrow \pi^*$ transitions frequently occur in the visible region for compounds which have the structural features (ii) and (iii) listed above. Some examples of coloured compounds with these features are shown in Fig. 9.



YELLOW



RED



ORANGE

Fig. 9. Some examples of compounds which are coloured due to the influence of extended conjugation and non-bonding electrons

In conclusion, colour in an organic compound normally arises because the energy of an electronic transition of the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ type falls within the range corresponding to visible radiation and the compound has the ability, in consequence, to absorb such radiation. The actual colour of the compound is dependent upon the wavelength range of the visible radiation absorbed, which in turn is dependent upon the structure of the compound.

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Synthesis of 1,3,5- and 1,4,5-trinitro- and 1,3,5,7- and 1,3,5,8-tetranitro-2,6-dimethylnaphthalenes

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Dimerisation of 2,4,6-trinitrotoluene (TNT) under the action of base yields 2,2',4,4',6,6'-hexanitrostilbene (HNS) in good yield,[1] this latter compound being of importance as a thermally stable explosive having applications in space technology.[2,3] Following a report[4] on a large laboratory scale preparation of 1,5-dinitro-2,6-dimethylnaphthalene (I), the authors have investigated the synthesis from this compound of trinitro- and tetranitro-2,6-dimethylnaphthalene which could have the potential for base-induced coupling to give thermally stable explosive materials analogous in structure to HNS.

The reaction of nitric acid and compound (I) in concentrated sulphuric acid gave 1,4,5-trinitro-2,6-dimethylnaphthalene (II) as follows. To a stirred solution of compound (I) (2g) in concentrated sulphuric acid (600cm^3) was added 0·6cm^3 of nitric acid ($d = 1·42$). After 2h the mixture was poured onto ice and the precipitated solid filtered off, washed thoroughly with water, dried *in vacuo*, and washed with toluene (15cm^3). Recrystallisation from glacial acetic acid gave compound (II) (1·54g), mp 193°C; n.m.r. spectrum (DMSO-d_6), τ 1·43 (1H, *s*), 1·99 and 2·03 (2H, AB_q, $J_{AB} = 9·0$ Hz), 7·39 (3H, *s*) and 7·46 (3H, *s*); mass spectrum, *m/e* 291 (M^+), 245 (base peak). The base peak corresponding to $[M\text{-}NO_2]^+$ showed that *peri*-nitro groups were present in the compound structure.[5]

The reaction of nitric acid with compound (I) in acetic anhydride yielded 1,3,5-trinitro-2,6-dimethylnaphthalene(III) as follows. To a stirred solution of compound (II) (5g), in acetic anhydride (300cm^3) was added 40cm^3 of nitric acid ($d = 1·42$) at a rate such that the temperature did not exceed 40°C. After the addition the solution was allowed to stand for 16h, and then 30cm^3 of nitric acid ($d = 1·50$) was added over a period of 4h, after which time 1·5cm^3 of concentrated sulphuric acid was added. The temperature of the reactant solution was slowly increased to 70°C while stirring continuously, and then after 5 min vigorous evolution of fumes the reactants were quenched in excess of water. (Caution has to be taken on heating owing to the formation of tetranitromethane in the reactant mixture.[6]) After 18h the precipitated solid was filtered off and recrystallised from acetone followed by acetic acid to give compound (III) (1·5g), mp 176°C; n.m.r. spectrum (DMSO-d_6), τ 1·40 (1H, *s*), 2·03 and 2·06 (2H, AB_q, $J_{AB} = 9·2$Hz), 7·45 (3H, *s*) and 7·48 (3H, *s*); mass spectrum, *m/e* 291 (M^+). The mass spectrum of compound (III) differed from that of the isomeric compound (II) in that the base peak did not correspond to $[M\text{-}NO_2]^+$ showing that there were no *peri*-nitro groups present.

Further nitration of compound (III) in fuming nitric acid/sulphuric acid yielded 1,3,5,8,tetranitro-2,6-dimethylnaphthalene (IV) in the following manner: 4cm^3 of nitric acid ($d = 1·50$) was added dropwise with stirring to a solution of compound (III) (13g) in concentrated sulphuric acid (400cm^3) in a vessel fitted with a drying trap. After standing for 30h the reaction mixture was poured onto ice and the precipitated product thoroughly washed with water followed by acetone and then recrystallised three times from glacial acetic acid to give compound (IV) (6·0g), mp 302°C; n.m.r. spectrum (DMSO-d_6), τ 1·22 (1H, *s*), 1·24 (1H, *s*), 7·41 (3H, *s*) and 7·47 (3H, *s*); mass spectrum, *m/e* 336 (M^+), 290 (base peak). As before, the base peak corresponding to the $[M\text{-}NO_2]^+$ ion indicated the presence of *peri*-nitro groups.

The action of fuming nitric acid on compound (III) in acetic anhydride resulted in the formation of 1,3,5,7-tetranitro-2,6-dimethylnaphthalene (V). Thus, a solution of compound (III) (3g) in acetic anhydride (300cm^3) was treated in exactly the same manner as for the preparation of compound (III). Recrystallisation as specified above yielded compound (V) (0·3g), mp 332°C; n.m.r. spectrum (DMSO-d_6), τ 1·35 (2H, *s*), 7·48 (6H, *s*); mass spectrum, *m/e* 336 (M^+).

Dr B. C. Webb of the Rocket Propulsion Establishment, Ministry of Defence, is thanked for discussions.

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Photolytic Decomposition of Indapamide

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Received December 20, 1978, from the *School of Chemical and Physical Sciences, Kingston Polytechnic, Kingston upon Thames KT1 2EE, England, and ‡Servier Laboratories, Ltd., Greenford, Middlesex UB6 7PW, England. Accepted for publication February 7, 1979.

Abstract □ Photolytic decomposition of indapamide (I) in nitrogen-flushed methanol yields 3-sulfamoyl-4-chlorobenzamide (II), 2-methylindoline (III), semicarbazide (IV), and 1-(*N*-formamido)-2-methylindoline (V); in oxygen-flushed methanol, II–V, 1-aminocarboxymethyl-2-methylindoline (VI), 3-sulfamoyl-4-chlorobenzoic acid (VII), methyl-3-sulfamoyl-4-chlorobenzoate (VIII), and 2-(*N*-acetamido)-benzoic acid (IX) are formed. A comparison is made with thermal decomposition of I.

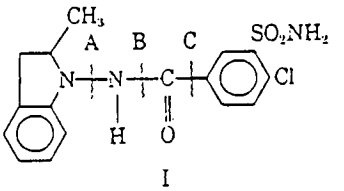
Keyphrases □ Indapamide—photolytic decomposition, thermal decomposition, decomposition products identified □ Photolysis—indapamide, products identified □ Thermolysis—indapamide, products identified □ Diuretics—indapamide, photolytic and thermal decomposition, products identified

There has recently been a growth in drug photosensitization studies. Numerous drugs have photosensitizing properties (1), and these properties appear to show a correlation with *in vivo* photosensitivity. In particular, the saluretic furosemide exhibits a high affinity for oxygen under UV irradiation, and this affinity may be related to the reported skin rash reaction among patients taking the drug (2).

As part of detailed studies of indapamide [*N*-(3-sulfamoyl-4-chlorobenzamido)-2-methylindole] (I), a compound with prolonged saluretic action (3), a study of the photolytic decomposition of this compound was conducted. In contrast to earlier studies (1), the products of *in vitro* photolytic decomposition were identified prior to *in vivo* experiments.

EXPERIMENTAL[1]

Indapamide (I) was supplied as a pure compound[2]. 2-Methylindoline (III), semicarbazide (IV), and 2-(*N*-acetamido)benzoic acid (IX) were supplied as pure reference compounds[3].



I

Photolytic decompositions were performed on 2.7×10^{-3} *M* I solution in nitrogen- or oxygen-flushed methanol. The reactant solutions were contained in the inner well of a cylindrical quartz reaction vessel, which was mounted vertically before a 1000-w Hanovia medium-pressure mercury lamp. A filter solution of saturated aqueous copper sulfate was pumped through the annular space (4-mm i.d.) surrounding the inner well of the reaction vessel and also was pumped through a heat-exchanger to maintain the reactant solution at 293°K. The filter solution had a short wavelength cutoff at 300 nm. After photolysis for 12 hr, the solution was evaporated to dryness under reduced pressure. The residue was dissolved in a small volume of redistilled methanol prior to spotting on TLC plates.

Thermal decompositions were performed by heating samples in an automatic thermo-recording balance[4]. A 1-g sample of I was heated either at a constant rate of 5°K/min from ambient temperature to 453°K until the weight loss rate stabilized or at 453°K for 12 hr while the sample underwent a regular and continuous weight loss. The solids were dissolved in redistilled methanol prior to spotting on TLC plates.

Preparative TLC was performed using 20 × 20-cm plates coated with a 1-mm layer of silica gel[5]. Two solvent systems were used for plate development: 1, 100% dimethyl carbonate; and 2, the top layer obtained after vigorously shaking pentan-1-ol (85 cm³) and ammonia (specific gravity 0.880, 15 cm³) together and then allowing them to stand. All solvent systems were prepared fresh daily, and not more than two developments were carried out in any one preparation.

After development, reactant and product spots were visualized under UV light, scraped off the plates, and extracted into a small volume of redistilled methanol, which was evaporated to dryness under reduced pressure. The residual material was identified spectroscopically.

RESULTS AND DISCUSSION

The results relating to the identification of the products formed by photolysis are summarized in Table I. These products arise principally as a result of bond cleavages in the N–NH–CO–C linkage.

[1] Mass spectra were recorded on an A.E.I. MS9 spectrometer, IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer, NMR spectra were recorded on a Perkin-Elmer R.10 spectrometer, and UV spectra were recorded on a Unicam SP 8000 spectrophotometer.

[2] Les Laboratories, Servicer, Gidy, France.

[3] Servier Laboratories, Greenford, Middlesex, England.

[4] Stanton.

[5] Merck GF_{254}.

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Table I—Products from Photolytic and Thermal Decomposition of Indapamide

Photochemical Decomposition in N_2-Flushed Methanol	Photochemical Decomposition in O_2-Flushed Methanol	Thermal Decomposition	Product R_f Value[a]	Method of Structure Assignment[b]
II	II	II	0.19[c]	NMR, IR, UV, and mass spectra
III	III	III[d]	0.65	Comparison of IR, UV, and mass spectra with those of a reference sam
		IV	0.75	Comparison of IR, UV, and mass spectra with those of a reference sam
		V[d]	0.26	UV and mass spectra
VI	VI	VI	0.19[c]	NMR, IR, UV, and mass spectra
VII[e]	VII[e]		0.35	Mass spectrum[f]
	VIII[e]		0.45, 0.44*	Mass spectrum[f]
	IX		0.12*	Comparison of IR, UV, and mass spectra with those of a reference sam
	X		0.65	NMR, IR, UV, and mass spectra
	XI[e]		0.27*	Mass spectrum[f]

[a] The R_f values refer to qualitative TLC plates developed in Solvent System 1, except for those marked with an asterisk, which refer to Solvent System 2. [b] Unless otherwise stated, spectra were obtained for products isolated from each of the three decomposition systems. [c] The product at R_f 0.19 was a mixture of II and VI. Compound was sublimed out of the mixture and obtained as a white crystalline compound. [d] Product only observed in those thermal decomposition samples maintained at 45° for 12 hr. [e] Minor product as judged by quantity of material isolated from TLC plates as compared to other products. [f] Only sufficient material could be isolated for mass spectrum to be recorded.

Type A cleavage leads to 3-sulfamoyl-4-chlorobenzamide (II and III), type B cleavage leads to 3-sulfamoyl-4-chlorobenzoic acid, and type C cleavage yields 1-(*N*-formamido)-2-methylindoline (V) and 1-aminocarboxymethyl-2-methylindoline (VI). Methyl-3-sulfamoyl-4-chlorobenzoate (VIII) presumably arises as a consequence of esterification of VII by the solvent, while IX arises as a consequence of indoline ring oxidative cleavage in species such as III or I. At present, the origin of IV is not clear.

Thermal decomposition of I yields only II–IV besides 2-methylindole (X) and *N*-(3-sulfamoyl-4-chlorobenzamido)-2-methylindole (XI). Thus, type A cleavage can occur from vibrationally excited levels of the ground (S_0) state, and II and III can arise by this mechanism in photolytic reactions. Such species could be generated by internal conversion from the photolytically generated S_1 state. Presumably, the appropriate S_0 levels for dehydrogenation are not accessible *via* internal conversion. Type B and C cleavages only occur under photolysis and must, therefore, arise from the first excited states. Since such reactions are not inhibited by oxygen, which is known to quench triplet-state molecules (4), the S_1 state is implicated.

Thus, the study has demonstrated the complexity of photolysis of a simple pharmaceutical and has shown the wide range of compounds to be screened in photosensitization tests of such molecules.

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ACKNOWLEDGMENTS

The authors thank Mr. D. Sen for experimental assistance.

Pestic. Sci. 1979, 10, 171–176

Photochemistry of Some Systemic Pyrimidine Fungicides[a]

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(Manuscript received 5 November 1978)

Synopsis

The compounds dimethirimol (I) (5-butyl-2-dimethylamino-6-methylpyrimidin-4-ol, and ethirimol (II) (5-butyl-2-ethylamino-6-methylpyrimidin-4-ol) are effective as fungicides for the control of powdery mildew on cucurbits and cereals respectively.[1,2] An understanding of the effect of ultraviolet (u.v.) radiation on agricultural chemicals is of importance and therefore, a study into the photochemistry of compounds I and II and also the structurally related 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (III) has been carried out.

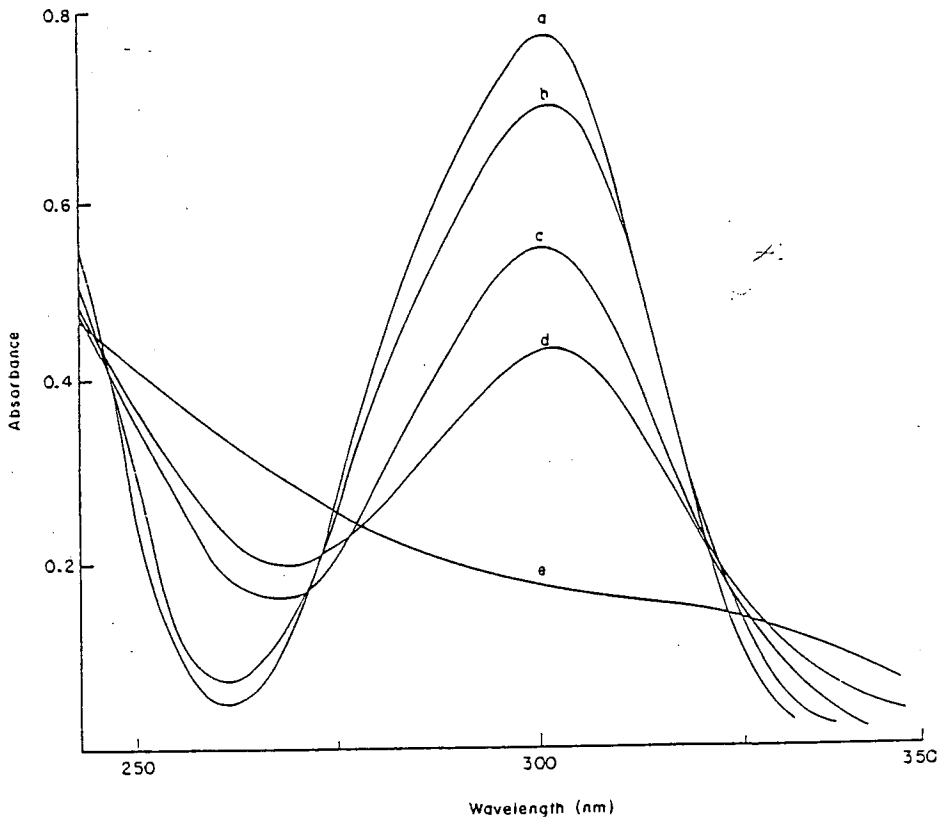

Figure 1. Absorption spectrum of a 0.4 mM degassed solution of dimethirimol (I) in acetonitrile (a) before photolysis, after photolysis for (b) 6 h; (c) 15 h; (d) 20 h; (e) 30 h.

[a] Synopsis of a paper presented at the symposium on *Photodegradation of pesticides* on 3 October 1978, organised by the Physicochemical and Biophysical Panel (Pesticides Group), Society of Chemical Industry.

0031–613X/79/0400–0171 $02.00

Photolysis of compounds I–III in degassed acetonitrile solutions with mercury radiation in range 290–330 nm brought about photochemical reaction as indicated by the disappearance with time of the longest wavelength absorption band of the substrate. A typical set of absorption spectra recorded after different photolysis times is shown in Figure 1. Separation of photolysis reaction products from the compounds I–III by thick-layer chromatography on silica gel gave four products for each of the three compounds. The products were identified by spectroscopic and degradation studies as being formed by dimerisation across the 5,6-bond of the parent pyrimidinol. The structures of the four products formed from compound I are shown in Figure 2.

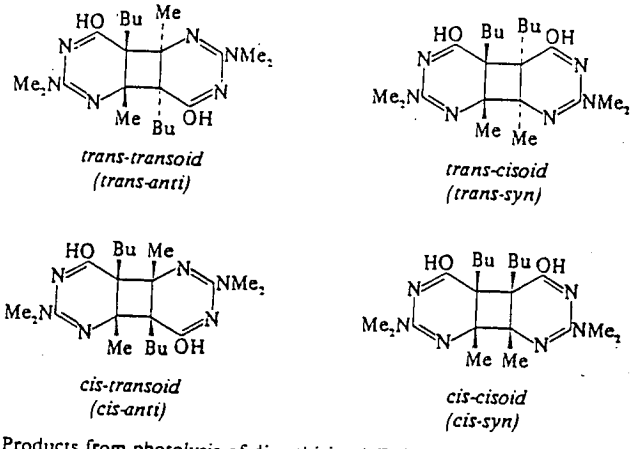

Figure 2. Products from photolysis of dimethirimol (I) in degassed acetonitrile solution.

Monitoring the disappearance with time of compounds I–III on photolysis in degassed acetonitrile gave plots which are typified by that shown for compound I in Figure 3. The effect of added *cis*-penta-1,3-diene on the photoreaction of I is also shown in Figure 3, where it can be seen that the added diene virtually completely quenched the reaction. The same effect was observed for the photolysis of II and III in the presence of *cis*-penta-1,3-diene. Gas–liquid chromatography (g.l.c.) analysis of the reaction mixtures revealed that *trans*-penta-1,3-diene had been formed as a result of the photolysis. As *cis*-penta-1,3-diene does not absorb at the wavelengths used for irradiation it is apparent that energy transfer from the pyrimidinol had brought about the *cis-trans* isomerisation of penta-1,3-diene. As the energy of the lowest excited singlet state of *cis*-penta-1,3-diene is con-

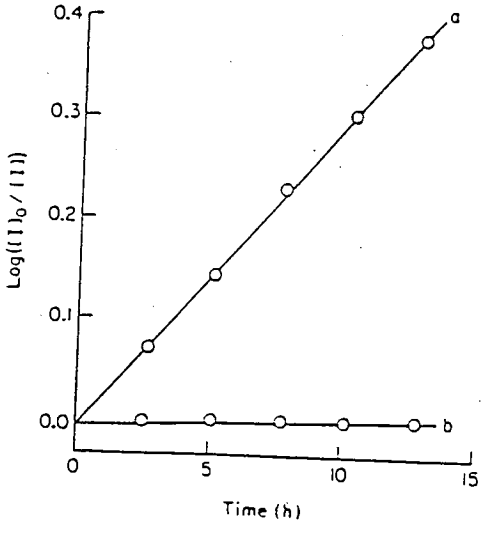

Figure 3. First-order kinetic plots for photolysis of a 0.5 mM degassed solution of dimethirimol (I) in acetonitrile in (a) the absence of *cis*-penta-1,3-diene and (b) the presence of *cis*-penta-1,3-diene (10.0 mM).

siderably higher than that of compounds I–III, singlet-singlet energy transfer was an unlikely mechanism for quenching of the photoreactions. Because the *cis-trans* isomerisation of penta-1,3-diene can proceed via a triplet state diene species,[3] it can be concluded that the quenching of the photoreactions of I–III in degassed acetonitrile occured by triplet energy transfer to the diene and, therefore, that the photoreactions of I–III in this medium proceeded via the lowest triplet state of compounds I–III.

The phosphorescence emission from the lowest triplet state of compounds I–III in EPA glass (diethyl ether + isopentane + ethanol, 5 + 5 + 1 by volume, at 77 K) is shown in Figure 4. The energies of the lowest triplet states as estimated from the O→O transitions (indicated by arrows on the spectra) were found to be as follows: I, 291 kJ mol^{-1}; II, 305 kJ mol^{-1}; III, 295 kJ mol^{-1}.

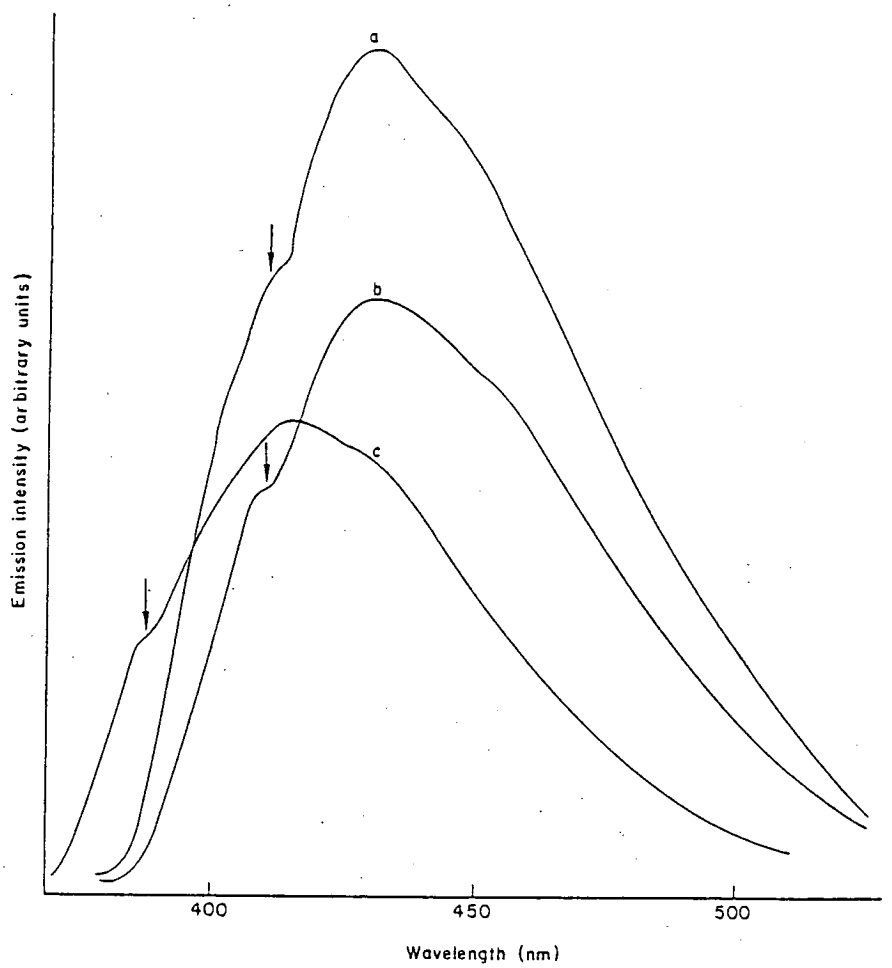

Figure 4. Phosphorescence spectra in diethyl ether + isopentane + ethanol (5 + 5 + 1 by volume) at 77 K of (a) dimethirimol (I); (b) ethirimol (II); (c) compound III. Excitation wavelength 300 nm.

The fluorescence and phosphorescence emissions from compounds I–III in cyclohexane + isopentane at 77 K corresponded to the fluorescence and phosphorescence emissions in aqueous solutions at pH 7 (Figure 5). This suggests that the emitting species in the aprotic solvent system was the same as that in the protic solvent system at pH 7. As only the neutral pyrimidinol species is likely to exist to any extent in the aprotic solvent, it is most probable that compounds I–III exist as neutral molecules in aqueous solution at pH 7. The fluorescence and phosphorescence

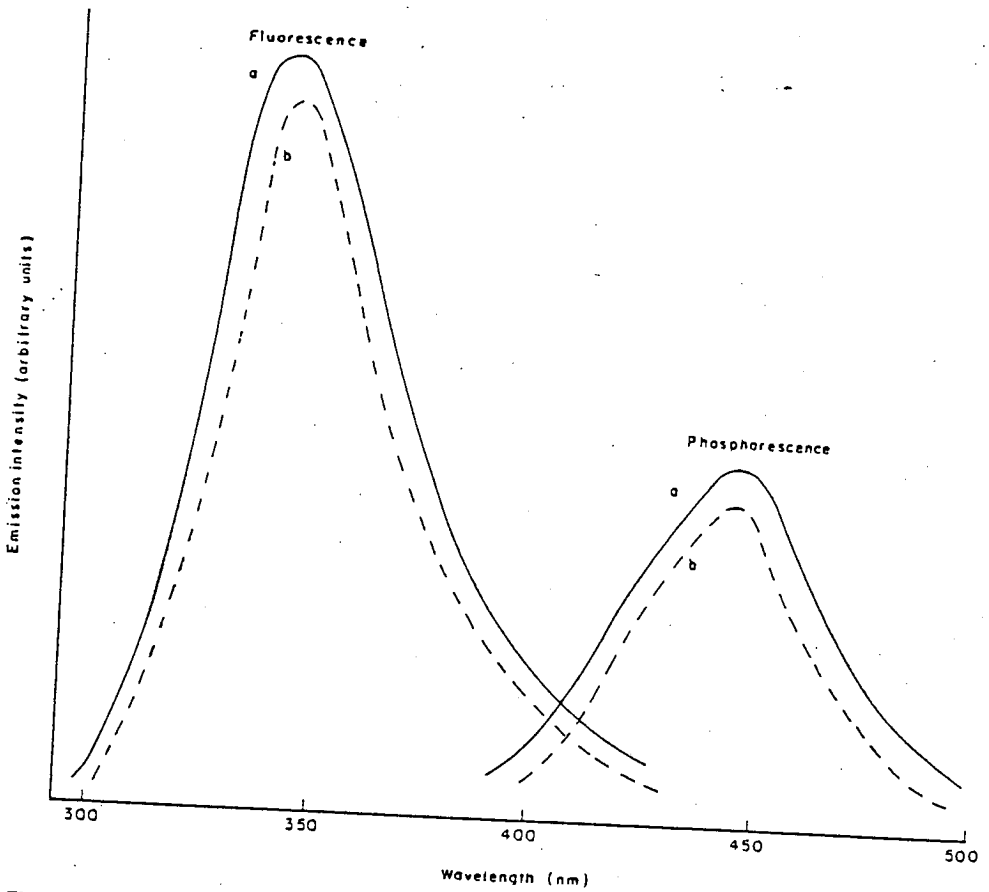

Figure 5. Fluorescence and phosphorescence spectra of (III) at 77 K in (a) cyclohexane: isopentane; (b) water at pH 7. Excitation wavelength 290 nm.

spectra of compounds I–III at low and high pH differ from those at pH 7 indicating the presence of cationic and anionic pyrimidinol species at low and high pH respectively.

Photolysis of compound III in degassed aqueous solution at pH 7 in the temperature range 278–333 K gives rise to two out of the four dimers formed in acetonitrile solution. It was reported previously in the case of the analogous four dimers produced on photolysis of thymine (5-methylpyrimidine-2,4-diol) and uracil (pyrimidine-2,4-diol) that the *cis*-isomers predominated at all reaction temperatures and were more stable than the *trans*-isomers.[4,5] In fact for thymine in an ice matrix the sole photo-product was the *cis-cisoid* dimer (*cis-syn* dimer).[4,5] Thus it may be concluded tentatively that the two products isolated in the present work are the *cis*-isomers.

Applying the steady-state approximation method to a simple reaction scheme, in which the parent pyrimidinol is consumed solely by reaction of triplet with ground state pyrimidinol to form dimers, results in the following expression

$$1/\bar{\Phi} = [1 + (k_d/k_r[\mathrm{Pyr}]_0)]/\Phi_{ISC} \qquad (1)$$

where $\bar{\Phi}$ is the quantum yield for consumption of pyrimidinol (calculated by monitoring the removal of pyrimidinol from the reaction system), Φ_{ISC} is the quantum yield for intersystem crossing from the singlet to triplet manifold of excited states, $[\mathrm{Pyr}]_0$ is the initial concentration of pyrimidinol, and k_d and k_r are the respective rate constants for unimolecular radiationless decay of the triplet state and the reaction of triplet state with ground state pyrimidinol.

A plot according to equation 1 is shown for compound III in Figure 6. It can be seen from Figure 6 that a straight line relationship holds at high values of $1/[\mathrm{Pyr}]_0$, that is at low initial pyrimidinol concentrations (<0.1 mM). Furthermore, the data obtained at three temperatures over the range

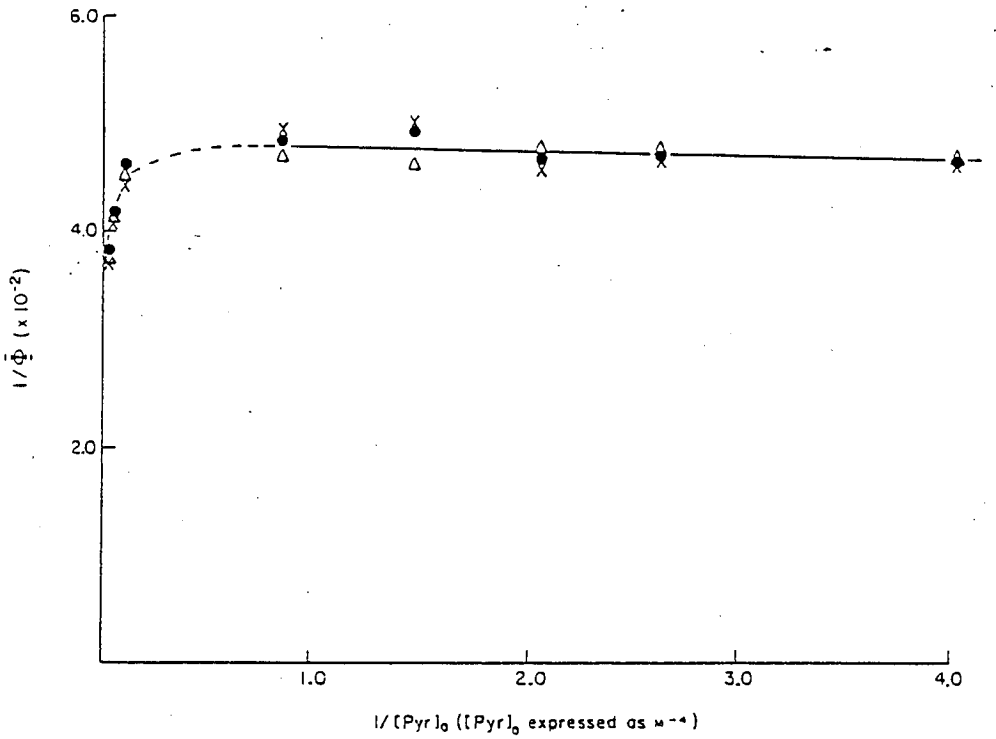

Figure 6. Plot according to equation 1 for dimerisation of compound (III): at 278 K, ×; 303 K, △; 333 K, ●.

278–333 K fall on the same straight line. It may be concluded, therefore, that the proposed mechanism holds at low pyrimidinol concentrations and that under these conditions photodimerisation proceeds via interaction of triplet with ground state pyrimidinol.

As shown in Figure 6, the experimental points obtained at high initial pyrimidinol concentrations (> 5 mM) fall off the straight line and the value of $1/\underline{\bar{\Phi}}$ is less than predicted by the straight line relationship. That is, the quantum yield, $\underline{\bar{\Phi}}$, for consumption of the pyrimidinol is greater than that predicted if dimers were formed solely by reaction of triplet with ground state pyrimidinol. Hence an additional mechanism for dimerisation must be operative at high pyrimidinol concentrations. This has been observed in other pyrimidinol systems where it has been proposed that dimerisation can occur via ground-state paired aggregates.[6–9] In this situation, two ground state pyrimidinol molecules are suitably associated to form an aggregate in which permanent bonding occurs to give a dimer on absorption of ultraviolet radiation. This is represented schematically as follows:

$$\text{Pyr} + \text{Pyr} \rightleftharpoons (\text{Pyr}.\text{Pyr}) \xrightarrow{h\nu} \text{Dimers}$$

If the above additional mode of forming dimers is taken into account in the reaction mechanism, a modified version of equation 1 is obtained, as follows:

$$\underline{\bar{\Phi}}_{\text{overall}} = \underline{\bar{\Phi}} + 2K[\text{Pyr}]_0\underline{\bar{\Phi}}^{A} \qquad (2)$$

where $\underline{\bar{\Phi}}_{\text{overall}}$ is the overall quantum yield for the consumption of pyrimidinol, $\underline{\bar{\Phi}}$ is the quantum yield for consumption of pyrimidinol via the triplet state alone, K is the equilibrium constant for the formation of aggregates, and $\underline{\bar{\Phi}}^{A}$ is the quantum yield for formation of dimers via aggregates. Results obtained at three different temperatures are plotted according to equation (2) in Figure 7. The straight line relationships so obtained support the conclusion that at high pyrimidinol concentrations (> 5 mM), dimersation via aggregates contributes to the overall dimerisation reaction. This is supported by the fact that the value of $\underline{\bar{\Phi}}$ overall decreases as the temperature is increased (Figure 7). This can be explained in terms of aggregates being 'shaken apart' at higher temperatures and, as a consequence, a lower proportion being able to form dimers as the temperature is increased.

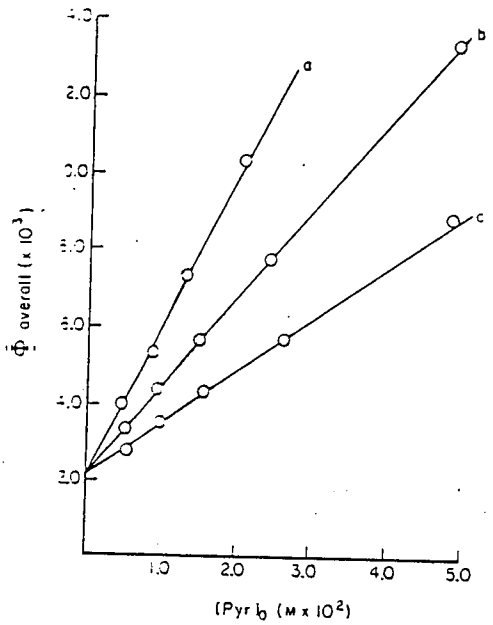

Figure 7. Plot according to equation 2 for dimerisation of compound (III) at (a) 278 K; (b) 303 K; (c) 333 K.

Acknowledgement

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Reaction of base with 1,3,8-trinitro and 1,3,6,8-tetranitro-2,7-dimethoxynaphthalene

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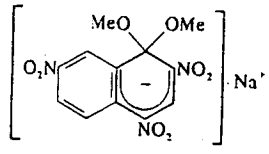
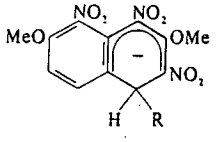
The action of base on α-TNT to produce the thermally stable explosive 2,2',4,4',6,6'-hexanitrostilbene is one of the most commercially important reactions involving the reaction of [1-3]base with an alkyl substituted polynitroaromatic compound. Numerous other analogous systems have been studied, [4-6] the majority of which have involved the reactions of base with alkoxy substituted polynitroaromatic compounds. [7-12] Most of the latter studies have been concerned with the reaction of base with 1-methoxy-polynitrobenzenes and 1-methoxy-polynitronaphthalenes. This work has shown that for reactions involving methoxide ion as base, addition of the methoxide ion occurs at either the *C*-1 or *C*-3 positions of the polynitro-aromatic with the thermodynamically favoured *C*-1 addition compound being obtained as the final stable product. In the case of the reaction of sodium methoxide with 1-methoxy-2,4,7-trinitronaphthalene addition occurs only at the *C*-1 position to give the 1,1-dimethoxy complex (I). [12] The reaction of methoxide ion with polynitro 1,5- and 1,7- dimethoxynaphthalenes also results solely in addition (unpublished results).

The authors have studied the reaction of methoxide-d_3 ion and sulphite ion with 1,3,8-trinitro-2,7-dimethoxynaphthalene (II) and 1,3,6,8-tetranitro-2,7-dimethoxynaphthalene (III) using n.m.r. spectroscopy and now report that addition of base occurs at position 4 to give anions having the structures (IV) and (V) respectively. Thus, in contrast to previous studies the thermodynamically favoured product is formed by addition of the base at a ring site which does not possess a methoxy substituent.

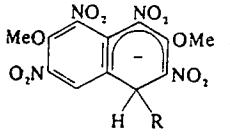
The reactions involving methoxide-d_3 were performed by adding the base to a solution of the parent compound in [$^2H_6$]-dimethyl sulphoxide and immediately recording the n.m.r. spectrum of the reactant solution. Thus, addition of one equivalent of sodium methoxide-d_3 to a solution of compound (II) in [$^2H_6$]-dimethyl sulphoxide resulted in the following n.m.r. spectrum assignable to anion (IV*a*): τ 6.14 (3H, *s*), 6.03 (3H,*s*), 4.44 (1H, *s*), 2.94 and 2.49 (2H, AB_q, J_{AB} 9.0Hz). The visible absorption spectrum obtained on diluting a solution which gave the n.m.r. spectrum of anion (IV) showed a single peak of λ_{max} 455nm. The peak maximum is in the region expected for anions of this type.[21]



(I)



(IV*a*) R = OCD_3
(IV*b*) R = SO_3^-



(V*a*) R = OCD_3
(V*b*) R = SO_3^-

Reactions involving sulphite ion were performed in D_2O/[$^2H_6$]-dimethyl sulphoxide mixtures. Thus, addition of three equivalents of sodium sulphite in D_2O to a solution of compound (III) in [$^2H_6$]-dimethyl sulphoxide gave the following n.m.r. spectrum: τ 4.34 (1H, *s*) and 1.85 (1H,*s*) with the resonance region of the methoxy substituents obscured by ^1H absorption of the solvent mixture. The visible absorption spectrum obtained on diluting a solution which gave this n.m.r. spectrum showed a peak of λ_{max} 458nm.

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Emission and absorption spectra of some substituted 4-hydroxypyrimidines

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Abstract—The fluorescence, phosphorescence and absorption spectra of 5,6-dimethyl-2-dimethylamino-4-hydroxypyrimidine (1), 5-*n*-butyl-2-dimethylamino-4-hydroxypyrimidine (2), and 5-*n*-butyl-2-ethylamino-4-hydroxypyrimidine (3) have been obtained in organic media and in aqueous solution at different pH values. The spectra reveal that the pyrimidines exist principally as cations at low pH, neutral species at pH values around 7 and as anions at high pH. The pK values for the ground state of compounds (1)–(3) have been measured as have the pK^* values for the first excited singlet state.

INTRODUCTION

The photochemical behaviour of the pyrimidines thymine (2,4-dihydroxy-5-methylpyrimidine) and uracil (2,4-dihydroxypyrimidine) is of great interest because of the role these pyrimidines play in the photodenaturation of nucleic acids [1–5]. As a consequence of this role, the spectroscopic properties of these and related compounds have been well documented [2,5–10]. The structural relationship of 5,6-dimethyl-2-dimethylamino-4-hydroxypyrimidine (1), 5-*n*-butyl-2-dimethylamino-4-hydroxypyrimidine (2) and 5-*n*-butyl-2-ethylamino-4-hydroxypyrimidine (3) to the nucleic acid pyrimidines has evoked interest in their photochemistry [11, 12], especially as compounds (2) and (3) are used as systemic fungicides [13, 14]. Knowledge of the photochemical behaviour of compounds (1)–(3) is of value because of the likelihood of photochemical reactions occurring when they are exposed to sunlight under field conditions. In order to gain information on possible species involved in the photochemistry of compounds (1)–(3), their emission and absorption spectra have been investigated and the results are reported herein.

EXPERIMENTAL

Compounds (2) and (3) were supplied by the Plant Protection Division, I.C.I. Ltd., and were recrystallized twice from methanol prior to use. Compound (1) was prepared by an adaptation of the method of HULL *et al.* [15]. 1,1-Dimethylguanidine sulphate (27.2 g) was added to ethanolic sodium ethoxide, prepared by adding clean sodium (4.6 g) to redistilled absolute ethanol (150 cm^3). The mixture was shaken for 15 min., then ethyl-2-methylacetoacetate (28.8 g) was added and the solution allowed to stand for 18 h, after which time it was refluxed for 2 h, cooled, filtered and the filtrate evaporated to low volume, whence compound (1) crystallized as needles. Recrystallization from methanol yielded product (8.4 g), m.p. 169–173°.

Fluorescence and phosphorescence spectra were recorded using a Perkin–Elmer/Hitachi MPF4 spectrometer. U.v. absorption spectra were recorded using a Unicam SP8000 spectrophotometer. Absorbance measurements were made using a Pye–Unicam SP6-500 and Perkin–Elmer Coleman 55 spectrometer. The u.v. absorption spectra were obtained at various pH values in triple distilled water and in a number of non-aqueous solvents. The pH values of the solutions were adjusted using 1 or 0.1 M hydrochloric acid (Hopkins and Williams, volumetric), and 1 or 0.1 M sodium hydroxide (Hopkins and Williams, volumetric). The spectra were recorded immediately after adjustment of pH and the pH of the solutions were measured before and after recording the spectra and an average pH value thus obtained.

RESULTS AND DISCUSSION

Data for the wavelength of maximum fluorescence and phosphorescence emission of compounds (1)–(3) are listed in Table 1. It can be seen from the table that for all three compounds the λ_{max} values

Table 1. Wavelength maxima (λ_{max}) for fluorescence and phosphorescence emission

Compound	pH	Fluorescence* λ_{max} (nm) 77 K†	298 K†	Phosphorescence‡ λ_{max} (nm) 77 K§
1	1.91	388	387	
	4.32	365	372	435
	5.51	360	365	
	7.00	358	365	430
	8.92	350	360	
	10.11	350	356	420
	11.64	350	356	
	13.40	350	360	
2	1.91	385	385	
	4.32	385	375	430
	5.51	380	370	
	7.00	375	365	425
	8.92	375	365	
	10.11	375	362	415
	11.64	375	362	
	13.40	360	360	
3	1.91	360	365	
	4.32	360	360	430
	5.51	355	360	
	7.00	355	358	430
	8.92	365	358	
	10.11	365	360	415
	11.64	365	356	
	13.40	335	356	

* Solvent—water.
† Excitation wavelength—290 nm.
‡ Solvent—ethylene glycol : water (1 : 1 v/v).
§ Excitation wavelength—300 nm.

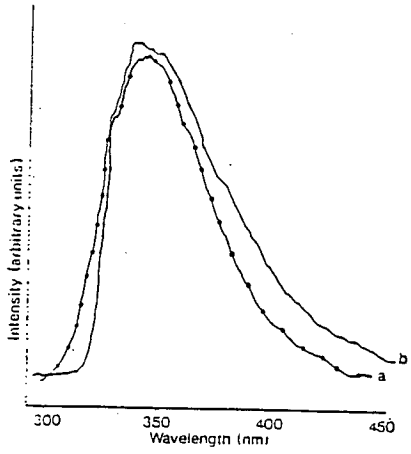


Fig. 1. Fluorescence spectra of compound (1) at 77 K in: (a) cyclohexane:isopentane (1:5 v/v), and (b) aqueous solution at pH = 7.02.

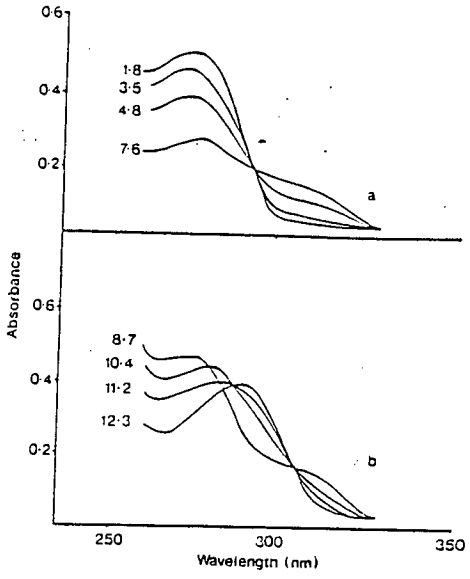


Fig. 2. Absorption spectra of compound (1) (0.96×10^{-3} M) in aqueous solution over pH ranges: (a) 1.8–7.6, and (b) 8.7–12.3.

for fluorescence and phosphorescence decrease as the pH increases, indicating that different species are acting as principal emitters in different pH regions. The bathochromic shift of the fluorescence λ_{max} values when the temperature is changed from 77 to 298 K is consistent with previous observations on the fluorescence spectra of nucleic acid pyrimidines [2].

The fluorescence spectrum of compound (1) in aqueous solution at pH = 7.02 is shown in Fig. 1, along with the fluorescence spectrum in cyclohexane:isopentane. The close similarity between the fluorescence spectra in the two solvent media, which was also observed for the fluorescence emission of compounds (2) and (3), is paralleled by the close similarity between the phosphorescence spectra of these compounds in ethylene glycol:water at pH = 7.00 and in cyclohexane:isopentane. These observations suggest that for each of the compounds the same species is emitting in the protic and aprotic solvent systems. Since it is unlikely that these pyrimidine compounds would be present in any form other than a neutral molecule in an aprotic solvent system such as cyclohexane:isopentane, it may be concluded that these pyrimidines exist mainly as neutral species in aqueous solution at pH values close to 7.

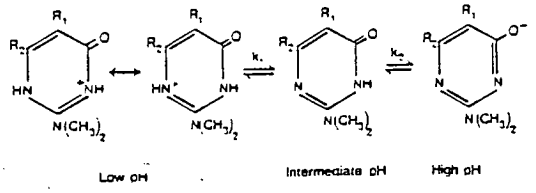
The u.v. absorption spectra of compound (1) at different pH values are shown in Fig. 2. Similar spectra were obtained for compounds (2) and (3). The figure shows that over the low pH range there is an isosbestic point at 290 nm whilst over the high pH range there is an isosbestic point at 309 nm. These observations taken in conjunction with the observations on the fluorescence and phosphorescence spectra indicate the existence of two single equilibria in the low and high pH ranges. This is explainable in terms of a cationic pyrimidinol species being present at low pH and an anionic pyrimidinol species at high pH with these species being in equilibrium with the neutral pyrimidinol

Table 2. Spectral and ionization data

Compound	pH	Species	λ_{max} (nm)	ε ($cm^2\ mol^{-1}$)	Isosbestic points (nm)	Ground state pK_1†	Ground state pK_2†	First excited singlet state pK_1^*‡	First excited singlet state pK_2^*‡
1	1.00	Cation	270	79,200	290	4.19	10.13	3.13	8.69
	7.00	Neutral	275 (298§)	4850					
	12.00	Anion	290	6670	309				
2	1.00	Cation	272	79,500	291	4.60	10.79	3.86	9.55
	7.00	Neutral	277 (300§)	5010					
	13.00	Anion	290	6650	305				
3	1.00	Cation	269	79,500	285	4.46	10.72	5.21	10.05
	7.00	Neutral	276 (296§)	4910					
	12.10	Anion	283	6630	299				

† Determined by the method described by ALBERT and SERJEANT [16].
‡ Determined by the method described by WELLER [17] and VANOER DONCKT [18].
§ Inflection point.

which is itself the principal species present at intermediate pH values. The equilibria may be represented as shown in the following scheme



The absorption maxima and molar extinction coefficients of the cationic, anionic and neutral pyrimidinols are listed in Table 2. Also listed in the table are the ground state pK values for the equilibria shown in the scheme, along with the pK^* values for the equilibria when involving first excited singlet state molecules. As expected, there are relatively small differences in the ground state pK values of compounds (1)–(3), reflecting the minor structural differences between these compounds. It is of interest that the pK^* values of the first excited singlet state of compounds (1)–(3) are generally less than the corresponding ground state pK values. Thus, compounds (1)–(3) act as weaker bases in their first excited singlet state than in the ground state and this may be an important factor in relation to their photochemistry when these pyrimidines are excited into their singlet state manifold.

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Studies on Nitroaromatic Compounds. Part 8.† A Kinetic and Spectroscopic Study of the Reaction of Di- and Tri-ethylamine with 1,5-Dimethyl-2,4,8-trinitronaphthalene

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The reaction of 1,5-dimethyl-2,4,8-trinitronaphthalene with diethylamine and triethylamine in DMSO and in DMSO–MeOH solvent systems has been studied. ^{1}H N.m.r. investigations have shown that a benzyl type anion is formed due to hydrogen abstraction from the 1-methyl group of the nitroaromatic compound. Kinetic and thermodynamic data for the systems have been determined. The results are explained in terms of the difference in solvation of the two amines and the charged products and the difference in solvating ability of the solvent media used. The effect of added triethylammoniun chloride on the reaction of 1,5-dimethyl-2,4,3-trinitronaphthalene with triethylamine in DMSO has been studied and the change in kinetics is attributed to ion association between the added salt and the charged products.

KINETIC, thermodynamic, and structural investigations of the reaction of bases with nitroaromatic compounds have received considerable attention and a variety of products have been proposed including Meisenheimer complexes, radical ions, and carbanions.[1-6]

The kinetics of the reaction of 2,4,6-trinitrotoluene with base to give the 2,4,6-trinitrobenzyl anion has been investigated by various workers,[7-11] but only recently has there been a successful n.m.r. investigation of the formation of this anion in flow and static systems.[12] N.m.r. spectroscopy has also been used to show the formation of a benzyl type anion in the reaction of 1,5-dimethyl-2,4,8-trinitronaphthalene with methoxide ion.[13] As far as is known, no other evidence for the formation of benzyl type anions from alkylpolynitronaphthalenes has been reported.

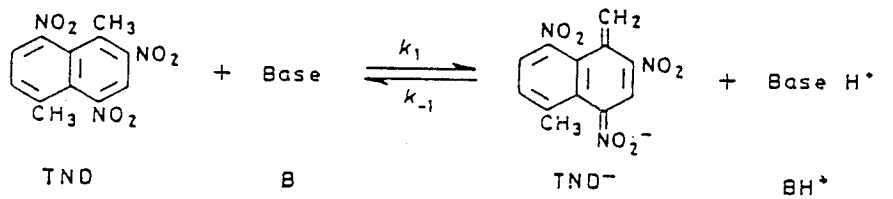
Previous studies of the reaction of amines with nitroaromatic compounds have indicated the formation of the zwitterionic form of a Meisenheimer complex and the conjugate base of this complex. For example, primary and secondary amines react with 2,4,6-trinitro-benzene and -anisole in DMSO to give a Meisenheimer complex with addition at C-1.[14-17] The reaction of butylamines with ethyl 2,4-dinitro-1-naphthyl ether in DMSO proceeds through an intermediate zwitterionic Meisenheimer complex by addition at C-1. The complex then loses a proton to the base to give the conjugate base of the neutral zwitterionic form.[18] Recently a flow n.m.r. study of this system confirmed the presence of the intermediate complexes.[19]

The present paper reports on the formation of a benzyl type anion in the reaction of diethylamine and triethylamine with 1,5-dimethyl-2,4,8-trinitronaphthalene (TND) in DMSO and DMSO–MeOH solvent systems.

† Part 7 is ref. 13.

RESULTS

Spectroscopy.—The ^{1}H n.m.r. spectrum of a mixture of TND and one equivalent of triethylamine in [$^2H_6$]dimethyl sulphoxide exhibited a set of product peaks which were assigned to the benzyl type anion, TND^-, shown in the Scheme. No peaks attributable to products other than those of the Scheme were observed in the spectrum. A similar ^{1}H n.m.r.. spectrum was obtained for the product



SCHEME

formed when diethylamine was added to TND in [$^2H_6$]-dimethyl sulphoxide. The product resonances in these spectra were in similar positions to those reported for the product formed on reaction of TND with methoxide ion.[13]

^{1}H N.m.r. spectroscopy showed that the reactions did not go to completion when methanol was present in the solvent system. Thus, the ^{1}H n.m.r. spectrum of a reaction system containing TND and three equivalents of triethylamine in a 3 : 1 mixture of [$^2H_6$]dimethyl sulphoxide–[$^2H_4$]methanol exhibited peaks due to both TND and TND^-. Addition of further [$^2H_4$]methanol to the system shifted the equilibrium position as evidenced by an increase in the relative intensity of the peaks due to TND and a concomitant decrease in intensity of the peaks due to TND^-. That is, the equilibrium constant for the system shown in the Scheme decreases as the methanol content of the solvent increases.

Visible absorption spectra of mixtures of TND and either di- or tri-ethylamine are typified by that shown in Figure 1. Since neither the reactants or the BH^+ species absorb in the visible region, the band with $\lambda_{max.}$ at 560 nm can be assigned to the TND^- anion. The values obtained for the molar decadic absorptivity, ε, of this species at 560 nm by reacting TND with excess of diethylamine and substituting the final absorbance (Abs) into the expression (Abs) = $\varepsilon[TND]_0 l$ are 1 970, 1 960, and 1 940 m^2 mol^{-1} at 303.5, 314.0, and

324.5 K, respectively. There is good agreement between these values and the respective values of 2 000, 1 970, and 1 940 $m^3 mol^{-1}$, determined at the same temperatures, from

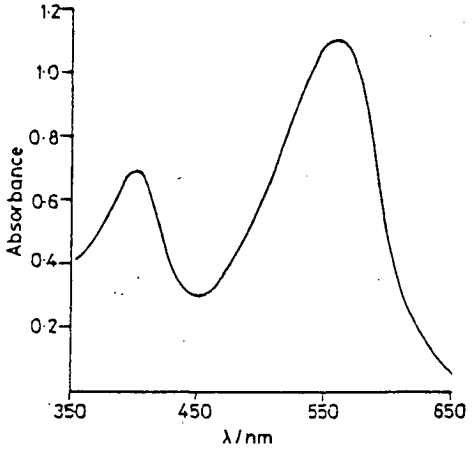


FIGURE 1 Absorption spectrum of a solution containing TND (6.8×10^{-5}M) and 800 equiv. of diethylamine in DMSO–MeOH (2 : 1). Cell path length $l = 10$ mm

Benesi–Hildebrand type plots on the results of the reaction of TND with an excess of triethylamine. A point of note is that the values for ε decrease with increase in temperature, a trend which has previously been reported for the values of ε for the charge-transfer complex formed between hexamethylbenzene and tetracyanoethylene.[20]

Kinetics.—Kinetic results were obtained by monitoring the change with time of the absorbance due to the TND^- anion at 560 nm. Kinetic analyses were then carried out using the appropriate equations given in the Experimental section. In the majority of cases the initial concentration of base was in excess, usually between 100 and 1 600 times the initial concentration of TND, so that pseudo-first-order kinetics applied to the forward reaction and second-order kinetics to the reverse reaction of the Scheme. For this situation, the pseudo-first-order rate constant, k_{obs}, for the forward reaction was evaluated using either equations (1) or (2). The values of k_{obs} for the reaction of TND with diethylamine and with triethylamine in different solvent systems are listed in Tables 1 and 2 respectively.

The second-order rate constant, k_1, for the forward reaction is related to k_{obs} by the expression $k_{obs} = k_1$[Base], and the values for k_1 listed in Tables 1 and 2 were obtained from the slope of the straight line plots of k_{obs} *versus* [Base].

Values for the equilibrium constant, K for the reaction of TND with base under various conditions are also listed in Tables 1 and 2. These values were derived using equations (3) or (4), or, in the case of solvent containing 67% DMSO, from the ratio of k_1/k_{-1}. Typical plots according to equation (4) are shown in Figure 2. The values for the second-order reverse rate constant, k_{-1}, given in Tables 1 and 2 were derived in most cases from the relationship $k_{-1} = k_1/K$. In

TABLE 1

Kinetic data for reaction of TND with diethylamine

t/°C	% DMSO by vol. in solvent	10^5[TND]/M	10^3[$HNEt_2$]/M	$10^3 k_{obs}/s^{-1}$	k_1/$dm^3 mol^{-1} s^{-1}$	k_{-1}/$dm^3 mol^{-1} s^{-1}$	K
21.4	100	5.11	5.11	1.93	0.37	0.45	0.82 [a]
		5.11	10.22	3.81			
		5.11	15.30	5.62			
30.5	100	5.11	5.11	3.01	0.59	0.89	0.65 [a]
		5.11	5.11	3.12			
		5.11	5.11	3.13			
		5.11	10.22	5.93			
		5.11	15.30	9.33			
41.4	100	5.11	5.11	5.38	0.97	1.67	0.59 [a]
		5.11	5.11	5.50			
		5.11	10.22	10.30			
		5.11	10.22	10.23			
		5.11	15.30	15.10			
		5.11	15.30	14.50			
31.5	67	6.82	6.82	0.792	0.112	0.86 [b]	0.130 [c]
		6.81	13.60	1.44			
		6.80	34.00	4.00			
		6.78	54.30	5.99			
41.0	67	6.82	3.41	0.588	0.210	2.35 [b]	0.089 [c]
		6.82	6.82	1.16			
		6.81	13.60	2.89			
		6.78	54.30	11.00			
51.5	67	3.41	3.41	1.14	0.36	5.99 [b]	0.060 [c]
		6.81	13.60	4.83			
		6.80	34.00	12.26			
30.5	50	5.11	10.22	0.567	0.06	0.50	0.12
		5.11	15.30	0.882			
		5.09	50.90	3.02			
		5.09	50.90	3.10			
41.0	50	5.11	5.11	0.405	0.088	3.14	0.028
		5.11	10.20	0.784			
		5.11	15.30	1.26			
		5.10	30.60	2.66			
		5.09	50.90	4.11			
52.3	50	5.11	10.22	1.97	0.213	10.00	0.021
		5.11	15.30	2.98			
		5.09	50.90	10.82			

[a] Value determined using low base concentrations. [b] Value determined using equation (5). [c] Value determined from k_1/k_{-1}.

TABLE 2

Kinetic data for the reaction of TND with triethylamine

t/°C	% DMSO by vol. in solvent	10^4[TND]/M	10^3[NEt_3]/M	$10^3 k_{obs}/s^{-1}$	k_1/dm^3 mol^{-1} s^{-1}	k_{-1}/dm^3 mol^{-1} s^{-1}	K
30.0	100	5.11	5.11	0.441	0.081	0.64	0.126
		5.11	10.22	0.862			
		5.09	40.07	3.34			
		5.06	80.93	6.53			
40.8	100	5.11	5.11	0.864	0.133	1.13	0.118
		5.11	10.22	1.62			
		5.11	10.22	1.63			
		5.10	20.40	3.05			
		5.09	40.70	6.12			
		5.06	80.93	10.20			
		5.06	80.93	11.05			
51.3	100	5.11	2.56	0.684	0.268	3.01	0.089
		5.11	3.83	1.08			
		5.11	5.11	1.41			
		5.11	10.22	2.82			
		5.11	10.22	2.80			
		5.10	25.50	6.82			
60.3	100	5.11	2.56	1.19	0.449	4.93	0.091
		5.11	5.11	2.18			
		5.11	5.11	2.41			
		5.11	10.22	4.59			
31.3	90	4.60	4.60	0.275	0.068	0.51	0.134
		4.60	9.20	0.621			
		4.60	10.50	0.782			
		4.59	23.00	1.59			
		4.58	36.70	2.42			
		4.57	54.80	3.77			
		4.56	72.90	4.96			
41.0	90	4.60	4.60	0.507	0.113	1.40	0.081
		4.60	11.49	1.28			
		4.58	36.70	4.14			
52.0	90	4.60	4.60	0.877	0.201	4.18	0.048
		4.60	11.49	2.41			
		4.58	36.70	7.91			
		4.56	72.90	14.40			
31.6	80	5.11	5.11	0.241	0.049	0.702	0.070
		5.11	10.22	0.453			
		5.10	20.40	1.09			
		5.09	40.70	2.07			
		5.07	60.90	3.02			
		5.06	81.00	3.94			
31.5	67	6.82	5.11	0.176	0.038	2.28 [a]	0.0167 [b]
		6.81	6.81	0.201			
		6.81	10.22	0.273			
		6.79	27.20	0.827			
		6.78	40.70	1.52			
		6.77	54.20	2.07			
41.0	67	6.82	5.11	0.216	0.070	6.84 [a]	0.0079 [b]
		6.81	10.22	0.497			
		5.10	20.40	1.09			
		5.07	60.90	3.28			
51.5	67	6.82	5.11	0.383	0.117	17.8 [a]	0.0066 [b]
		6.81	10.22	0.815			
		6.79	27.20	2.47			
		5.09	40.70	3.68			
		5.07	60.90	5.62			
60.3	67	6.82	6.82			32.3 [a]	
32.0	50	5.11	10.22	0.182	0.021	4.88	0.0043
		5.11	15.30	0.300			
		5.10	20.40	0.455			
		5.09	30.60	0.611			
		5.08	50.80	1.06			
41.0	50	5.11	10.22	0.217	0.027	15.9	0.0017
		5.09	30.60	0.868			
		5.08	50.80	1.33			
52.3	50	5.11	10.22	0.635	0.070	25.9	0.0027
		5.09	30.60	2.17			
		5.68	50.80	3.50			

[a] Value determined using equation (5). [b] Value determined from k_1/k_{-1}.

those systems where the solvent contained 67% DMSO, values for k_{-1} were determined using equation (5).

Arrhenius plots for the change with temperature of k_1 and

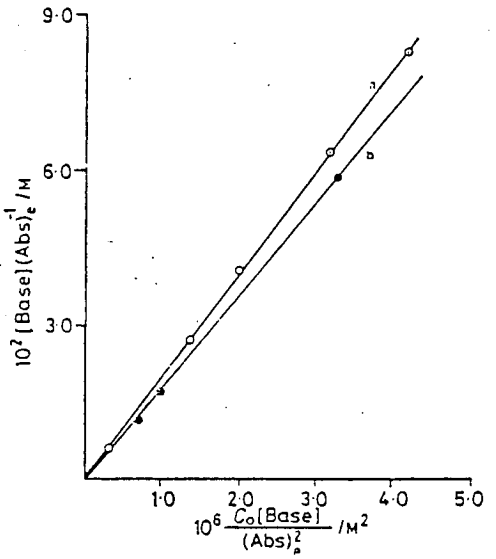


FIGURE 2 Benesi–Hildebrand plots according to equation (4) for the reaction of TND with (a) triethylamine in DMSO–MeOH (9 : 1) at 304.3 K, and (b) diethylamine in DMSO–MeOH (1 : 1) at 303.5 K

k_{-1} in different solvent mixtures gave good straight lines. Values for the enthalpy of activation, $\Delta H^{\ddagger}$, and entropy of activation, $\Delta S^{\ddagger}$, calculated from such plots are listed in Table 3. Also listed in certain cases are the calculated values for the overall enthalpy change, ΔH, and the overall entropy change ΔS, for the two reaction systems.

Kinetic data for the reaction of TND with triethylamine in the presence of triethylammonium chloride are given in Table 4.

TABLE 4

Kinetic data for the reaction of TND (5.12×10^{-5}M) with triethylamine in DMSO at 313.4 K in the presence of triethylammonium chloride (5.12×10^{-3}M)

10^2[Et_3N]/M	$10^3 k_{obs}$/s^{-1}	k_1 [a]/dm^3 mol^{-1} s^{-1}	k_{-1}/dm^3 mol^{-1} s^{-1}
0.512	0.661	0.129	0.076,[b] 0.067 [c]
1.024	1.350	0.132	
8.190	9.910	0.121	

[a] Derived from expression $k_f = k_{obs}$/[Base]. [b] Derived from expression $k_{-1} = k_1/K$ where the value of K as determined experimentally using equation (7) is 1.67. [c] Determined by addition of triethylammonium chloride (5.12×10^{-3}M) to a previously equilibriated mixture of TND (5.12×10^{-5}M) and triethylamine (1.02×10^{-3}M) followed by analysis using equation (9).

DISCUSSION

Tables 1 and 2 show that the rate constants, k_1, for the forward reaction increase as the percentage of DMSO in the solvent system increases, whilst Figure 3 shows that a reasonably linear relationship is observed when log k_1 is plotted against % DMSO. The rate constants, k_{-1}, for the reverse reaction decrease as the percentage of DMSO is increased although the results for the composition range 90—100% DMSO are not entirely consistent with this behaviour.

Generally in the formation of Meisenheimer complexes from lyate ions and nitroaromatic compounds in DMSO–ROH solvent mixtures, the increase in the forward rate constant as the amount of DMSO is increased is attributed to the enhanced nucleophilicity of the lyate ion which results from the lower solvation of the ion as the percentage of DMSO increases,[3,5,6] whilst the decrease in the reverse rate constant is attributed to the enhanced solvation of the Meisenheimer complex in solvents containing a high percentage of DMSO.[5] Normally when anions react with aromatic molecules in Meisenheimer complex formation or in nucleophilic displacement reactions, $\Delta H^{\ddagger}$ decreases and $\Delta S^{\ddagger}$ often increases as the percentage of DMSO in the solvent increases.[21,22] However the opposite trend in $\Delta H^{\ddagger}$ was observed for the reaction between hydroxide ion and 2,4-dinitrophenyl 3-nitrophenyl ether.[23]

In the present study of hydrogen abstraction by a neutral base from a nitroaromatic compound, the increase in k_1 with increase in the DMSO content of the solvent for the reaction of TND with triethylamine appears to be due to an increase in $\Delta S_1^{\ddagger}$, as indicated by the trend in $\Delta H_1^{\ddagger}$ values (see Table 3). However, for the reaction with diethylamine the corresponding increase in k_1 appears to be due to a decrease in $\Delta H_1^{\ddagger}$. For both reactions the decrease in k_{-1} as the percentage of DMSO increases is due to a large decrease in $\Delta S_{-1}^{\ddagger}$ compensating for a decrease in $\Delta H_{-1}^{\ddagger}$.

An interesting feature of the results given in Table 3 is that for the reaction of TND with both di- and triethylamine the overall enthalpy change, ΔH, is more exothermic in mixed solvent than in 100% DMSO. This can be explained on the basis that there is a greater degree of solvation of products in the mixed solvent than in 100% DMSO, with the greater solvation arising because of hydrogen bonding between methanol in the mixed solvent and nitro-groups carrying a partial

TABLE 3

Thermodynamic parameters for the reaction of TND with di- and tri-ethylamine in DMSO–MeOH at 298 K

Base	% DMSO	$\Delta H_1^{\ddagger}$/ kJ mol^{-1}	$\Delta H_{-1}^{\ddagger}$/ kJ mol^{-1}	ΔH/ kJ mol^{-1}	$\Delta S_1^{\ddagger}$/ J K^{-1} mol^{-1}	$\Delta S_{-1}^{\ddagger}$/ J K^{-1} mol^{-1}	ΔS/ J K^{-1} mol^{-1}
Et_2NH	100	34.9 ± 3.0	48.4 ± 4.0	−13.5 ± 5.0	−135 ± 6	−87 ± 8	−48 ± 10
	67	45.6 ± 3.0	76.0 ± 3.5	−30.4 ± 4.6	−113 ± 6	3 ± 7	−117 ± 9
	50	45.2 ± 4.5			−120 ± 10		
Et_3N	100	45.9 ± 3.0	56.4 ± 4.0	−10.5 ± 5.0	−115 ± 6	−63 ± 8	−52 ± 10
	90	40.4 ± 4.0	82.3 ± 4.0	−41.9 ± 5.7	−135 ± 8	12 ± 8	−147 ± 11
	67	43.7 ± 3.0	81.0 ± 3.5	−37.3 ± 4.6	−129 ± 6	28 ± 7	−157 ± 9
	50	47.0 ± 4.5			−124 ± 10		

The standard state in $\Delta S^{\ddagger}$ calculations taken as 1 mol dm^{-3}.

negative charge in the product species.[23,24] Thus, the greater release of energy arises because hydrogen bonding stabilises the system relative to the situation where hydrogen bonding does not occur. The fact that the overall entropy change, ΔS, for the two reactions are much more negative in mixed solvent than in 100% DMSO is consistent with the foregoing in that there will be a lesser degree of freedom for product molecules and a more ordered system produced in the mixed solvent.

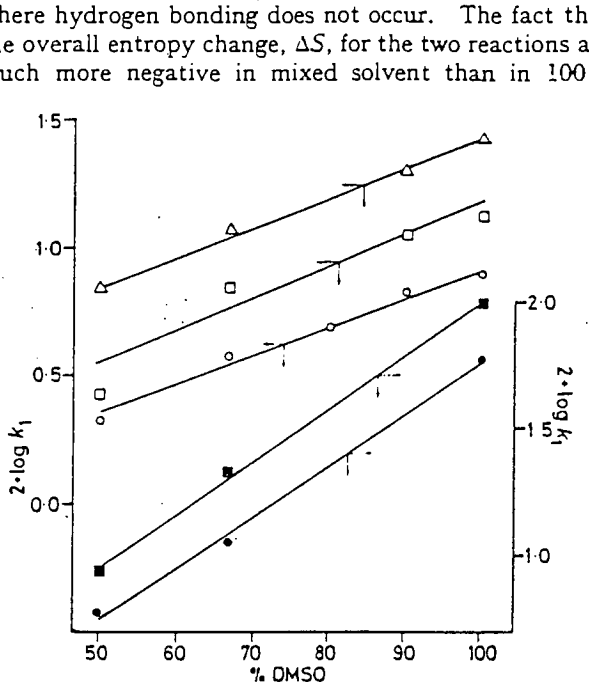


FIGURE 3 Plots of log k_1 against % DMSO in solvent for reaction of TND with (a) diethylamine at 303.5 (●) and 314 K (■), and (b) triethylamine at 304.5 (○), 314 (□), and 325 K (△)

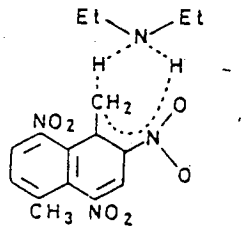
It is noteworthy that in 67% DMSO the overall entropy change is less negative for the reaction with diethylamine than for that with triethylamine. The most likely explanation is that in the former reaction system hydrogen bonding occurs between the amine hydrogen of diethylamine and the methanol in the mixed solvent [25] and, as a consequence, diethylamine is solvated to a greater extent than triethylamine. This would lead to a smaller decrease in entropy on forming products from the TND–diethylamine system than from the TND–triethylamine system.

The large negative values for the entropy of activation, $\Delta S_1^{\ddagger}$, for the forward step in the reaction of TND with both of the amines in the different solvent systems indicates that the activated complex is more highly ordered than the reactants. It is of interest that the values for the entropy of activation given in Table 3 are similar to the value of -134 J K^{-1} mol^{-1} determined for the reaction of n-butylamine with ethyl 2,4-dinitro-1-naphthyl ether in DMSO to form a zwitterionic Meisenheimer complex by addition at C-1.[18]

The value of $\Delta S_1^{\ddagger}$ for the reaction of TND with diethylamine in 100% DMSO is more negative than the corresponding value for the reaction with triethylamine. Since solvation of the reactants in the two systems will be similar in 100% DMSO, this result implies that there is a greater restriction imposed on the activated complex in the former situation. This could arise by the formation of the complex (X) which contains an eight-membered ring in which bonding occurs to the hydrogen atom of diethylamine. This conclusion supports the postulate previously put forward of involvement of an eight-membered cyclic transition state in hydrogen abstraction from 2,4,6-trinitrotoluene by sodium isopropoxide.[26]

The entropy of activation, $\Delta S_{-1}^{\ddagger}$, for the reverse reaction has positive values for the reactions carried out in mixed solvent and negative values for the reactions carried out in 100% DMSO (see Table 4). This is consistent with the expected large increase in entropy when during the course of the reverse reaction in mixed solvent, the activated complex is formed from the two highly solvated charged species TND^- and BH^+.

Comparison of the results presented in Table 4 for the reaction of TND with triethylamine in DMSO at 313.4 K in the presence of triethylammonium chloride with the corresponding results at 314.0 K in the absence of triethylammonium chloride (Table 2) shows that the effect of the added salt is to decrease the value of the reverse rate constant, k_{-1}, from 1.130 to 0.076 dm^3 mol^{-1} s^{-1} and to increase the value of the equilibrium constant from 0.12 to 1.67. These results parallel the observations of previous workers [6] who noted that in the formation



(X)

of a Meisenheimer complex by addition of methoxide ion to substituted dinitro-anisoles the value of K increased markedly with increase in concentration of sodium methoxide owing to an apparent decrease in k_{-1} values. Both sets of results are explainable in terms of the charged product, benzyl-type ion or Meisenheimer complex, being stabilised by ion association.

EXPERIMENTAL

1,5-Dimethyl-2,4,8-trinitronaphthalene (TND) was prepared and purified as previously described.[27] Reagent grade di- and tri-ethylamine were distilled using a Fischer Spaltrohr 60 theoretical plate column, the middle fractions being selected. Dimethyl sulphoxide (reagent grade), [$^2H_6$]dimethyl sulphoxide, AnalaR methanol, and [$^2H_4$]-methanol were dried over molecular sieve prior to use. Triethylammonium chloride was prepared by addition of concentrated hydrochloric acid to stirred triethylamine at 0 °C; the crystals formed on neutralisation were filtered off, twice recrystallised from absolute ethanol, and dried in *vacuo*.

90-MHz ^{1}H Continuous-wave n.m.r. spectra were recorded

at 31 °C on a Perkin-Elmer R32 spectrometer, whilst 90-MHz ^{1}H Fourier-transform n.m.r. spectra were recorded on the same instrument fitted with a Nicolet TT4 Fourier transform unit. 220-MHz ^{1}H continuous-wave n.m.r. spectra were recorded at PCMU, Harwell. Chemical shifts were measured relative to internal tetramethylsilane as reference. Dissolution of TND (0.021 g) in [$^2H_6$]dimethyl sulphoxide (0.5 cm^3) followed by addition of triethylamine (0.01 cm^3) and recording of the 220 MHz spectrum within 5 min gave the following spectrum for the benzyl type anion: τ 1.35 (1 H, s), 2.54 and 2.72 (2 H, ABq, J_{AB} 8 Hz), 4.09 (1 H, s), 5.12 (1 H, s), and 7.86 (3 H, s).

U.v.–visible absorption spectra were recorded on a Perkin-Elmer SP 1700 spectrophotometer using 10 mm matched silica cells in a thermostatted cell compartment maintained at ±0.1 °C. Reaction mixtures were prepared by mixing thermostatted solutions of TND with the appropriate amine in a cell capped with a PTFE stopper. To check that evaporation of the amine did not occur, the PTFE stopper was replaced by a silica-seal rubber cap in some runs and the amine injected through the cap by syringe. Identical results were obtained by each method. Reversal of the reaction was achieved by letting the reaction reach the equilibrium position, removing one-third of the solution from the cell, replacing with the same volume of methanol at the same temperature, the cell being rapidly shaken and replaced in the spectrophotometer. Reversal of the reaction was also achieved by adding 0.5 cm^3 of triethylammonium chloride (3.07×10^{-2}M) in DMSO to 2.5 cm^3 of an equilibrated mixture of TND (5.12×10^{-4}M) and triethylamine (1.023×10^{-2}M) in DMSO.

Treatment of Experimental Data.—In cases where pseudo-first-order kinetics applied to the forward reaction and second-order kinetics to the reverse reaction of the Scheme values for the pseudo-first-order rate constant, k_{obs}, were obtained from plots according to equation (1) where C_0

$$\ln\left[\frac{C_0C^- + C^-(C_0 - C_e^-)}{C_0(C_e^- - C^-)}\right] = \frac{(2C_0 - C_e^-)}{C_e^-}k_{obs}t \quad (1)$$

represents the initial concentration of TND, and C^- and C_e^- represent the respective concentrations of TND$^-$ at time t and at equilibrium. The reaction between TND and excess of diethylamine in DMSO proceeded virtually to completion and for this system equation (1) could be used in the simplified form (2).

$$-\ln(C_e^- - C^-) = k_{obs}t + \text{constant} \quad (2)$$

The concentration of TND$^-$ during a run was determined by monitoring the absorbance, (Abs), at 560 nm and substituting the absorbance values into the Beer–Lambert relationship $C^- = (Abs)/\varepsilon l$. The molar absorptivity, ε, of the TND$^-$ anion was determined from Benesi–Hildebrand type plots, according to either equations (3) or (4), with the latter equation being used in the majority of cases. The equilibrium constant, K, was also determined from these plots.

$$\frac{C_0}{(Abs)_e} = \frac{(Abs)_e}{[Base]\,K(\varepsilon l)^2} + \frac{1}{\varepsilon l} \quad (3)$$

$$\frac{[Base]}{(Abs)_e} = \frac{C_0[Base]\varepsilon l}{(Abs)_e^2} + \frac{1}{\varepsilon lK} \quad (4)$$

Since the reaction of TND with excess of diethylamine in DMSO proceeded to virtual completion under the conditions used for kinetic runs, the molar absorptivity, ε, could be obtained directly from the expression $C_0 = (Abs)_e/\varepsilon l$. However the equilibrium constant, K, had to be determined using lower base concentrations than those used in the kinetic runs. Typically a ratio of [Base]/C_0 of *ca.* 10 used, and the values of K were obtained by substitution of the measured value of $(Abs)_e$ into equation (3) or (4).

In a number of runs, reaction mixtures in DMSO were allowed to reach equilibrium and sufficient methanol was then added to give a final solvent composition containing 67% DMSO. Addition of the methanol resulted in a reversal of the forward reaction of the Scheme, and the resultant decrease in absorbance at 560 nm was followed with time. The kinetic expression applicable in these cases is given in equation (5) where C_0 is the concentration

$$\ln\left[\left\{\frac{C^- + C_0C_0/(C_0 - C_e^-)}{C^- - C_e^-}\right\}\left\{\frac{C_0^- - C_e^-}{C_0^- + C_e^-C_0/(C_0^- - C_e^-)}\right\}\right] = \frac{C_0 - C_e^-}{C_e^-(2C_0 - C_e^-)}k_{-1}t \quad (5)$$

of TND in the original DMSO solvent multiplied by a dilution factor of 2/3, C_0^- and C^- are the respective concentrations of TND$^-$ immediately after the addition of methanol and after time t and C_e^- is the concentration of TND$^-$ at the *final* equilibrium position. Values of k_{-1} were determined by plotting the left-hand side of equation (5) against t.

The reaction of TND with excess triethylamine in DMSO in the presence of triethylammonium chloride was investigated in a number of runs and was found to obey pseudo-first-order forward and first-order reverse kinetics. Plots based on equation (6) were used to derive values for the pseudo-first-order rate constant k_{obs} from which values for the rate constant k_1 were determined using the expression $k_{obs} = k_1$[Base]. The values of ε and K for these systems

$$-\frac{C_e^-}{C_0}\ln\left[1 - \frac{C^-}{C_e^-}\right] = k_{obs}t \quad (6)$$

were determined from Benesi–Hildebrand type plots according to equation (7) where [BH$^+$] represents the concentration of triethylammonium chloride.

$$\frac{C_0}{(Abs)_e} = \frac{[BH^+]}{K\varepsilon l[Base]} + \frac{1}{\varepsilon l} \quad (7)$$

Addition of triethylammonium chloride to a previously equilibrated mixture of TND and triethylamine in DMSO causes reversal of the forward reaction of the Scheme and a consequent decrease in the absorbance at 560 nm due to the TND$^-$ anion. The kinetic expression (8) applies to the approach to the new equilibrium position where C_0 is the

$$-\ln\left[\frac{C^- - C_e^-}{C_0^- - C_e^-}\right] = [BH^+]\left[1 + \frac{C_e^-}{C_0 - C_e^-}\right]k_{-1}t \quad (8)$$

initial concentration of TND corrected for dilution caused by addition of the solution of triethylammonium chloride in DMSO, C_0^- is the concentration of TND$^-$ at the first equilibrium position, and C^- and C_e^- are the respective concentrations of TND$^-$ at time t after the addition of triethylammonium chloride and at the *final* equilibrium position. The second-order rate constant, k_{-1}, for the reverse reaction was determined by monitoring the decrease in absorbance at 560 nm with time after the addition of

triethylammonium chloride and plotting the results according to the following modified form of equation (8)

$$-\ln(C^- - C_e^-) = ak_{-1}t + b \qquad (9)$$

where a and b are constants.

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Pestic. Sci. 1981, 12, 215–218

Rates of Reaction of Singlet Oxygen with Some Systemic Pyrimidine Fungicides and Related Compounds

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Rate constants have been measured for the reaction in chloroform solution of singlet oxygen with the fungicides ethirimol (5-butyl-2-ethylamino-6-methylpyrimidin-4-ol) and dimethirimol (5-butyl-2-dimethylamino-6-methylpyrimidin-4-ol), and with the compounds 2-dimethylamino-5,6-dimethylpyrimidin-4-ol, 2-dimethylamino-6-methylpyrimidin-4-ol, 4-benzyloxy-2-dimethylamino-5,6-dimethylpyrimidine and 2-diethylamino-6-methylpyrimidin-4-ol. The values obtained show that singlet oxygen reacts readily with these compounds; the differences between the rate constant values have been rationalised in terms of the different structural features of the compounds studied. The possibility that singlet oxygen may react with agricultural chemicals under natural conditions is considered.

1. Introduction

Many agricultural chemicals react in the environment under the influence of sunlight and oxygen to form oxidation products. For example, exposure of the fungicide ethirimol to sunlight yielded a complex range of products including a number of highly oxygenated species.[1] Although in many cases the structures of photo-oxidation products are known the mechanism whereby these products are formed and the role of oxygen in the photo-oxygenation process remains unclear.

Singlet oxygen ($^1O_2$) is a highly reactive form of molecular oxygen and can be produced readily by photosensitisation.[2–6] Many of the compounds which can sensitise the formation of singlet oxygen, including dyes,[5] porphyrins[7] and chlorophylls,[7] absorb in the visible region of the spectrum and hence have the capability of using the energy of the sun to produce singlet oxygen. As there is such a wide variety of compounds able to sensitise the formation of singlet oxygen, it is quite possible that singlet oxygen could be generated in the environment under conditions in which it can react with an agricultural chemical to give oxygenation products. The findings, that singlet oxygen can be generated by irradiation of sensitisers bound on surfaces and that the singlet oxygen so formed can undergo gas phase[3] and liquid phase[8–10] reactions, lend support to the possibility of singlet oxygen being involved in environmental reactions.

In order to test whether singlet oxygen might have a role in environmental photo-oxidations, determinations were made of the rate of reaction of singlet oxygen with the two fungicides ethirimol (I) and dimethirimol (II), and also the four structurally related compounds: 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (III), 2-dimethylamino-6-methyl-pyrimidin-4-ol (IV), 4-benzyloxy-2-dimethylamino-5,6-dimethylpyrimidine (V), and 2-diethylamino-6-methylpyrimidin-4-ol (VI), shown in Figure 1.

2. Materials and methods

Rubrene (Aldrich Chemical Co.) and chloroform (Hopkins and Williams Ltd. 'A' grade) were used as received. Compounds I–VI were prepared by procedures outlined previously.[11]

0031–613X/81/0400–215 $02.00

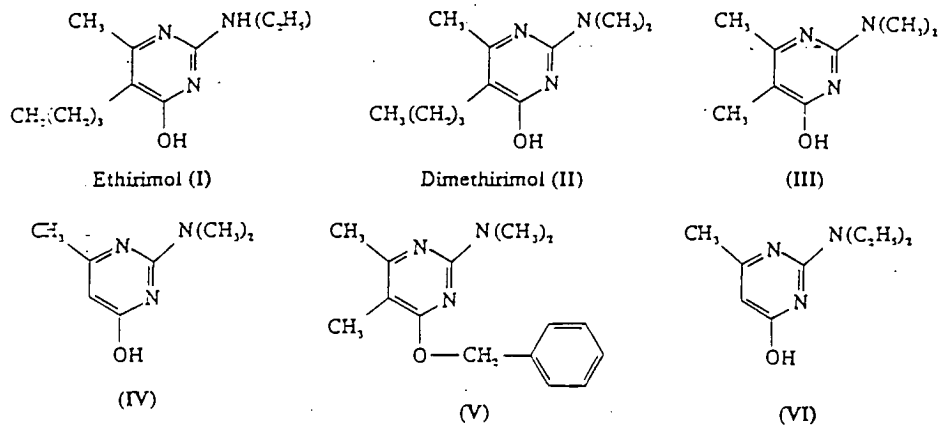

Figure 1. Ethirimol (I), dimethirimol (II) and the four structurally related compounds III–VI.

Stock solutions of rubrene (1.6 mM) were prepared by dissolving weighed amounts of rubrene in measured volumes of chloroform. Solutions containing compounds I–VI were prepared by dissolving weighed amounts of each in separate measured volumes of rubrene stock solution to give a final concentration of 20 mM for each compound. In this way, each solution for photolysis had the same initial concentration of rubrene and the same initial concentration of the compound under test.

Samples were prepared for photolysis by pipetting prepared solutions (5 ml) into quartz tubes (10 mm i.d.). To ensure that each sample received the same amount of radiation, the samples were simultaneously photolysed using a 60-W fluorescent light tube located in a quartz well at the centre of a 'merry-go-round' reactor.[12] All radiation from the fluorescent tube of wavelength shorter than 440 nm was filtered out using Chance–Pilkington OY8 filter glass. The samples were irradiated for 4.5 h, during which time approximately one-third of the rubrene had been consumed in the solutions not containing a pyrimidine compound. After irradiation, the sample solutions were diluted five-fold and the absorbance of the rubrene remaining in each solution was measured at 440 nm ($\epsilon = 233$ m^2 mol^{-1}) on a Unicam SP6-500 spectrophotometer.

3. Results and discussion

Rubrene is an orange hydrocarbon which on absorbing visible radiation both sensitises the formation of $^1O_2$ and reacts with $^1O_2$ according to the scheme:

$$R + h\nu \longrightarrow {}^1R \tag{1}$$

$$^1R \xrightarrow{k_2} {}^3R \tag{2}$$

$$^1R + {}^3O_2 \xrightarrow{k_3} {}^3R + {}^1O_2 \tag{3}$$

$$^3R + {}^1O_2 \xrightarrow{k_4} R + {}^1O_2 \tag{4}$$

$$^1O_2 \xrightarrow{k_5} {}^3O_2 \tag{5}$$

$$R + {}^1O_2 \xrightarrow{k_6} RO_2 \tag{6}$$

in which k represents the rate constant for the process shown, R is rubrene, ^1R is the rubrene first

excited singlet state, ^3R is the rubrene lowest triplet state and RO_2 is the colourless peroxide formed by addition of $^1O_2$ to rubrene.

If to this system is added a substrate P which either quenches singlet oxygen or reacts competively with R for singlet oxygen, then the following reaction has to be included in any kinetic-analysis:

$$P + {}^1O_2 \xrightarrow{k_R} \begin{matrix} P + {}^3O_2 \\ \text{products} \end{matrix} \qquad (7)$$

where k_R represents the overall rate constant for all interactions/reactions of P with singlet oxygen. If reaction (7) occurs, the rate of removal of rubrene from the system will be reduced, relative to that when no substrate P is added, because of the competition between P and R for $^1O_2$. It has been shown[13,14] that, if two solutions of equal volume, one containing substrate P and one without P and each having the same initial concentration of rubrene, are each exposed to the same amount of $^1O_2$, k_R can be calculated from the equation:

$$k_R = \{k_6([R]_F^P - [R]_F^O) + k_5 \ln([R]_F^P \mid [R]_F^O)\}/[P] \ln([R] \mid [R]_F^P) \qquad (8)$$

in which [R] is the initial concentration of rubrene, $[R]_F^P$ the final concentration of rubrene in the solution containing substrate P, $[R]_F^O$ the final concentration of rubrene in the solution not containing substrate P, and [P] the concentration of substrate P.

Values for the rate constants k_5 and k_6 have been determined[15,16] and when substituted into equation (8) the following expression is obtained:

$$k_R = \{5.3 \times 10^7([R]_F^P - [R]_F^O) + 1.7 \times 10^4 \ln([R]_F^P \mid [R]_F^O)\}/[P] \ln([R] \mid [R]_F^P) \qquad (9)$$

Equation (9) was used to determine values for the rate constant (k_R) for the reaction of singlet oxygen with compounds I–VI. The results, listed in Table 1, show that all the compounds reacted with singlet oxygen, the rates of reaction being comparable to the rates of reaction of singlet oxygen with a variety of organic substrates.[5,17,18] Singlet oxygen is an electrophilic reagent, and the observation that it reacts readily with compounds I–VI is in accord with these compounds being electron-rich because of the number of electron-donating substituents on the pyrimidine ring.

Table 1. Rate constants for the reaction of singlet oxygen with compounds I–VI

Compound	$k_R \times 10^6$ (mol^{-1} s^{-1})
I	2.26 (±0.22)
II	5.54 (±0.38)
III	11.5 (±0.11)
IV	1.03 (±0.02)
V	9.02 (±0.27)
VI	0.70 (±0.04)

Values are the average of three determinations.

A noteworthy feature of the results shown in Table 1 is that there is almost a ten-fold difference between the rates of reaction of III and IV. These two compounds differ structurally in that there are two methyl group substituents on the 5,6-double bond in III, whereas there is only one methyl group substituent in IV. This structural difference probably accounts for compound III being the more reactive, as it has been found previously[19] that the rate of reaction of singlet oxygen with methyl-substituted olefins correlates with the number of methyl groups on the olefinic double bond.

This effect arises because the greater the number of methyl groups, the more electron-rich the molecule becomes. In this respect, the higher rate of reaction of dimethirimol (II) as compared to ethirimol (I) most probably reflects the greater electron-donor ability of the dimethylamino group at C-2 in II as compared with the ethylamino group at C-2 in I.

Comparison of the rates of reaction of compounds II and IV, as given in Table 1, shows that the former is the more reactive; this was expected because II has an electron-donating butyl group at C-5 whereas IV does not. It is interesting that the rate of reaction of compound II is about one-half that of III, suggesting that the bulky nature of the butyl group at C-5 relative to that of a methyl group at C-5 sterically hinders attack by singlet oxygen. This conclusion is supported by earlier studies[20] on the reaction of singlet oxygen with a series of trialkyl-substituted olefins in which it was found that the relative reactivity decreased with increasing steric bulkiness of one alkyl group.

The results on the relative rates of reaction of compounds II–IV suggest that one site of attack of singlet oxygen on these compounds is at the 5,6-double bond. In this context, the small difference in the reaction rates for compounds III and V would suggest that C-4 is not a primary site of attack by singlet oxygen. The mode of attack of singlet oxygen on all six compounds is currently being investigated by separation and identification of the products formed. Preliminary work has shown that complex product mixtures are produced in agreement with previous findings that reaction of singlet oxygen with organic compounds can proceed by a number of different types of reaction with the formation of a variety of products.[3]

4. Conclusions

Singlet oxygen can react with the fungicides ethirimol (I) and dimethirimol (II), as well as the structurally related compounds III–VI; if singlet oxygen were formed under field conditions, reactions might be expected to occur with the fungicides (I) and (II), and possibly with any other agricultural chemicals present.

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Photo-dimers from the Photolysis of 2-Dimethylamino-5,6-dimethylpyrimidin-4-ol in Aqueous Solution

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Photolysis of 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (I) in degassed aqueous solution yields two isomeric photo-dimers which are formed by dimerisation across the 5,6-double bond of I. The yield of dimers is dependent upon the initial concentration of I and on the temperature; this can be explained in terms of a mechanism whereby pyrimidinol aggregates react to give dimers. The formation of aggregates can account for the fact that the quantum yield for the overall reaction of I was higher in degassed acetonitrile than in degassed aqueous solution, it can also account for four photo-dimers being formed in the former solvent and only two in the latter solvent. The photo-dimers revert to I when heated or on photolysis. That photo-dimers are not formed under natural conditions in the environment is considered to be partly because oxygen may react competitively with photo-excited pyrimidinol species and so prevent dimerisation.

1. Introduction

2-Dimethylamino-5,6-dimethylpyrimidin-4-ol (I) is a hydrolysis product of the pesticide pirimicarb, and because I may be formed in the environment, a knowledge of its photochemical behaviour is of interest. The photochemistry of I in degassed acetonitrile solution has been previously reported on, as has the photochemistry of the structurally related fungicides dimethirimol (5-butyl-2-dimethylamino-6-methylpyrimidin-4-ol; II), and ethirimol (5-butyl-2-ethylamino-6-methylpyrimidin-4-ol; III) in the same solvent system.[1–3] Compounds I–III react in degassed acetonitrile to produce four isomeric photo-dimers, these dimers being formed by self-addition across the 5,6-double bond of the parent pyrimidine. These dimers have not been detected, however, in crops, soils or water which were treated with the three compounds I–III and exposed to sunlight under natural conditions. In order to ascertain whether it is possible for photo-dimers to be formed in aqueous systems, a study of the photochemistry of I in degassed aqueous solution was undertaken, and the results are reported herein.

2. Materials and methods

Compound I was prepared by the method described previously.[2] [2-^{14}C]I was supplied by Plant Protection Division, ICI Ltd. Benzophenone and diphenylmethanol (Hopkins and Williams, Analar) were thrice recrystallised from ethanol prior to use. Water was deionised, triple distilled in glass apparatus and used immediately to make up solutions.

Absorption spectra were recorded on a Unicam SP8000 spectrophotometer and absorbance measurements were made using a Unicam SP6-500 spectrophotometer. Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Perkin-Elmer R32 spectrometer fitted with a Transform Technology 'Fourier Transform' accessory.

Samples were prepared for photolysis by pipetting sample solutions (3 ml) into 10-mm i.d. quartz tubes, connected by a graded seal to a Pyrex socket; the tubes were degassed by a repeated

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freeze-thaw cycle until a vacuum of at least 0.3 N m^{-2} was achieved, and then sealed *in vacuo*. Each sample was prepared in duplicate or triplicate. Up to 28 sample solutions were simultaneously photolysed using a 500-W Hanovia medium-pressure mercury arc lamp located in a quartz well at the centre of a 'merry-go-round' apparatus[4] which itself was located in a constant temperature bath. For photolysis, using radiation in the range 290–330 nm, the lamp radiation was filtered by means of a Chance OX7 glass filter (2 mm) in combination with a filter solution of potassium chromate (1.05 g in 2 litres of 1% aqueous sodium carbonate) pumped through the annulus in the quartz well and through a heat exchanger. This filter combination had a transmission maximum at 313 nm and cut-offs at 290 and 330 nm. After photolysis, the sample solutions were evaporated down to dryness under vacuum without the application of heat. The residues were taken up in a small volume of an appropriate solvent prior to analysis or further study.

Studies on the photodegradation of dimers were performed by photolysing aqueous solutions of dimers in an Applied Photophysics (London) 'merry-go-round' reactor using a 250-W medium-pressure mercury lamp as radiation source. The filter system used comprised (*a*) 2M-nickel(II) sulphate in 5% sulphuric acid (2 cm); (*b*) 0.8M-cobalt(II) sulphate in 5% sulphuric acid (2 cm); and (*c*) 0.4mM-iodine and 0.7 mM-potassium iodide in water (2 cm). This filter combination had a transmission maximum at 250 nm and cut-offs at 220 and 270 nm. Studies on the thermal degradation of the dimers were performed by maintaining the solutions under investigation at a known temperature in the thermostatted cell compartment of either a Unicam SP8000 or SP6-500 spectrophotometer, and monitoring the change with time of the absorbance at 300 nm.

Preparative thin layer chromatography (t.l.c.) was performed on Merck silica gel F_{254} plates (0.4 mm layer thickness × 20 cm × 20 cm), pre-washed with methanol, using chloroform + acetone + methanol (80 + 15 + 5 by volume) as eluant. Quantitative t.l.c. was performed using Kontes silica gel LQDF$_{254}$ plates (0.25 mm layer thickness × 20 cm × 20 cm) with pre-scored 2-mm divisions giving 19 strips on each plate. These plates had the advantage of a pre-absorbent layer, thus providing the means of rapidly applying quantitative amounts of a number of samples. Samples containing ^{14}C-labelled material were applied as streaks to the pre-absorbent layer and the solvent (chloroform + acetone + methanol; 80 + 15 + 5 by volume) allowed to run up the pre-absorbent layer until it reached the silica gel, whereupon the plate was removed and dried in an oven maintained at 303 K. The activity at the baseline was measured using a Geiger-Muller tube (Mullard ZP/481) held directly above the baseline region in a specially constructed mounting movable in the X-Y directions. After the radioactivity had been determined, the plate was developed three times using the same solvent system, the plate being dried as before between each development. After

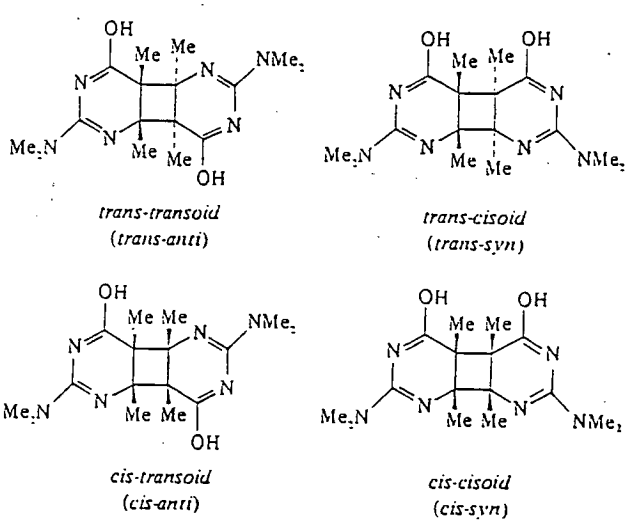

Figure 1. Possible photo-dimers from 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (pyrimidinol I).

development, the radioactivity in the regions corresponding to dimers was determined under the same conditions as the activity on the baseline. The yield of each dimer was calculated by expressing the radioactivity due to each dimer as a percentage of the initial activity reading at the baseline. The overall quantum yield ($\Phi_{overall}$) for the reaction of the pyrimidinol I was calculated using the following expression:

$$\Phi_{overall} = (\text{The number of pyrimidinol molecules that reacted})/(\text{the number of quanta incident upon the sample})$$

The numerator in this expression was evaluated by measuring the absorbance of the pyrimidinol at an appropriate wavelength before and after photolysis, and relating the change in absorbance to a change in pyrimidinol concentration, using the Beer–Lambert relationship and the pre-determined value of the molar extinction coefficient of pyrimidinol I at the chosen analytical wavelength, and in the particular solvent system used. The denominator in the above expression was evaluated by monitoring the intensity of radiation incident upon the samples during photolysis using the benzophenone-diphenylmethanol actinometer.[5–7]

3. Results and discussion

The structures of the four possible isomeric dimers, formed by dimerisation across the 5,6-double bond of pyrimidinol I, are shown in Figure 1. T.l.c. of the mixtures of products from the photolysis of I in degassed aqueous solution at 278 and 298 K, revealed that only two out of the four possible photo-dimers were formed. An autoradiogram showing the position of the two photo-dimers relative to that of the pyrimidinol I is represented in Figure 2; as can be seen, some activity remained on the baseline after plate development. At 278 K, the baseline material represented some 12% of the total product yield and it was found to be comprised mainly of 1,1-dimethylguanidine. Also shown in Figure 2 is a representation of an autoradiogram of the mixture of products from the photolysis of I in degassed acetonitrile solution. This autoradiogram shows that the four possible

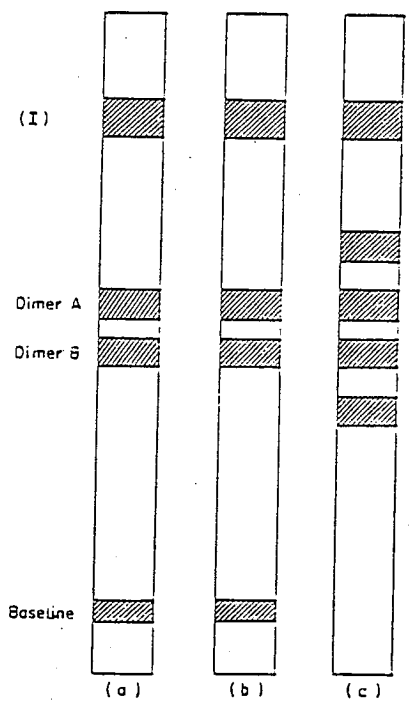

Figure 2. Autoradiograms of the mixtures of products from photolysis of the pyrimidinol I in (a) degassed aqueous solution at 278 K; (b) degassed aqueous solution at 293 K; and (c) degassed acetonitrile at 293 K.

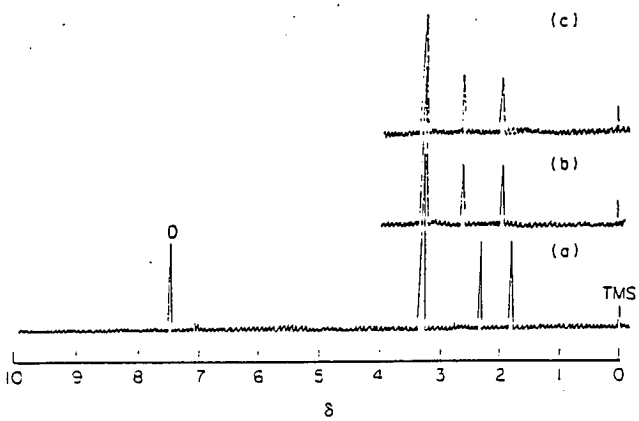

Figure 3. Nuclear magnetic resonance spectra in deuterochloroform of (a) the pyrimidinol I, (b) dimer A, and (c) dimer B. D = deuterochloroform: TMS = tetramethylsilane.

photo-dimers are formed in acetonitrile and that the two having intermediate R_F values correspond to the two dimers formed in aqueous solution.

The stereochemistry of the two photo-dimers formed in degassed aqueous solution is open to conjecture as it was not possible to obtain crystallographic or dipole moment data on these dimers as has been the case for the corresponding dimers formed from the structurally related pyrimidines thymine (5-methylpyrimidine-2,4-diol) and uracil (pyrimidine-2,4-diol).[8] As expected, the electron impact and chemical-ionisation mass spectra of the photo-dimers were the same as those of the parent pyrimidinol due to breakdown of the dimers into monomer under the thermal conditions used in the mass spectrometers. However, as shown in Figure 3, the n.m.r. spectra of the two photo-dimers differed from that of the parent pyrimidinol. Although the n.m.r. spectra are consistent with the proposed dimer structure, it is not possible to deduce the stereochemistry of the dimers from such spectra. However, it has been reported,[9] in the case of the analogous four dimers formed on photolysis of thymine in aqueous solution, that the *cis*-isomers predominated at all reaction temperatures between 275–343 K. In fact, for thymine in an ice matrix, the sole photo-product was the *cis-cisoid* dimer (*cis-syn* dimer).[10,11] These results suggest that the two dimers isolated in the present work are those with the *cis*-configuration.

Figure 4 shows how the yield of each dimer depended on the initial concentration of the pyrimidinol I and on the temperature over the range 278–333 K. It is of interest that the yield of dimer A is higher than that of dimer B at each of the three temperature used. Also of interest is the fact

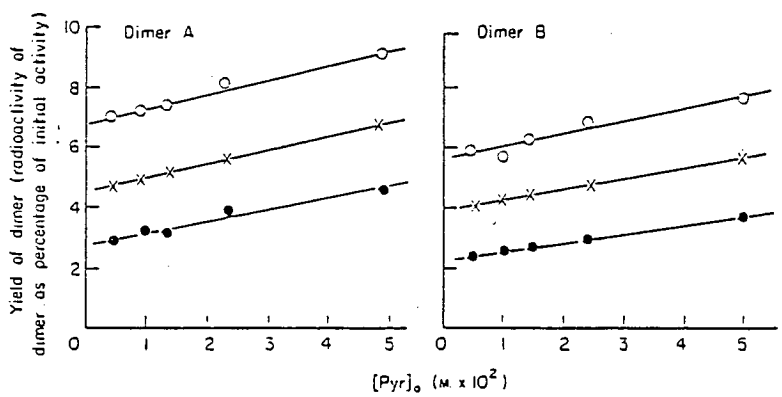

Figure 4. Yield of dimer (in the form of the radioactivity of the dimer, expressed as a percentage of the initial activity) as a function of the initial pyrimidinol I concentration, $[Pyr]_0$, and the temperature. ○, 278 K; X, 303 K; and ●, 333 K.

that the yield of dimer increases as the initial pyrimidinol concentration is increased. Earlier results[3] showed that at low initial pyrimidinol concentrations (< 5mM), dimers are formed solely by the reaction of triplet with ground state pyrimidinol species but that at higher pyrimidinol concentrations, dimers are formed by an additional mechanism which involves ground-state paired aggregates. This latter mechanism is represented below:

$$\text{Pyr} + \text{Pyr} \underset{\text{aggregate}}{\rightleftharpoons} (\text{Pyr.Pyr}) \xrightarrow{h\nu} \text{dimers}$$

The present results support the involvement of this mechanism in dimer formation, as it is to be expected that as the concentration of pyrimidinol increases, so the extent of aggregation will increase and thus the yield of dimers will also increase. This mechanism for dimer formation is also supported by the effect of temperature on dimer yield. It can be seen from Figure 4 that as the temperature is increased, so the yield decreases. This can be explained in terms of the aggregates having greater vibrational energy at the higher temperatures and breaking apart at higher temperatures, with the consequence that a lower proportion of aggregates will be able to react to form dimers as the temperature is increased.

The variation in the overall quantum yield ($\Phi_{overall}$), for the reaction of the pyrimidinol I as the composition of the solvent medium is changed from 100% water to 100% acetonitrile, is shown in Figure 5. The Figure shows that the quantum yield is higher in acetonitrile than in aqueous solution, and that furthermore, as shown in Figure 2, four dimers are formed in acetonitrile whereas only

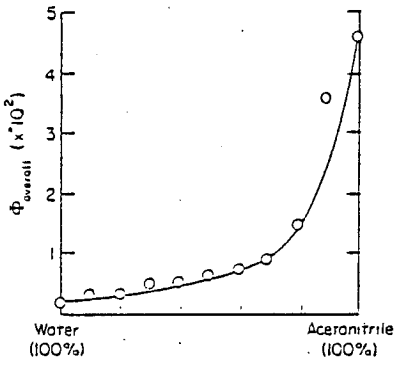

Figure 5. Variation of overall quantum yield ($\Phi_{overall}$), for reaction of the pyrimidinol I, with the composition of the aqueous acetonitrile solvent.

two are formed in aqueous solution. Obviously the solvent medium will have an effect on the extent of aggregation, and as the initial pyrimidinol concentration (10^{-3}M), in the experiments represented in Figure 5, is in the region where dimerisation via aggregates will have a significant role, the difference in quantum yield, between water and acetonitrile as solvents, may well arise because of the difference in the degree of aggregation in these two solvent systems. Water being highly polar would not be such a favourable medium for aggregate formation as acetonitrile, because the greater degree of solvation of the pyrimidinol moiety in water will make the energy barrier to aggregate formation relatively higher. The orientation of the pyrimidinol molecules in the aggregates will predetermine the stereochemical structure of the dimers and presumably, in water, only two out of the four possible orientations give aggregates which are sufficiently strongly bound to overcome the solvating effects of the aqueous medium. Thus, in aqueous solution, there will be only two types of aggregate that can react on absorption of radiation to give dimers.

The photo-dimers from the pyrimidinol I have similar properties to those formed from thymine and uracil in that they revert to the parent pyrimidinol when subjected to heat or ultraviolet radiation.[3] The formation of the pyrimidinol I can be monitored readily because its longest wavelength absorbtion band in water (λ_{max} 275 nm) is well removed from the corresponding absorption band of the dimers ($\lambda_{max} < 240$ nm). The formation with time of the pyrimidinol I, as measured by the increase in absorbance at 300 nm, when aqueous solutions of the dimers are heated at 358 K and

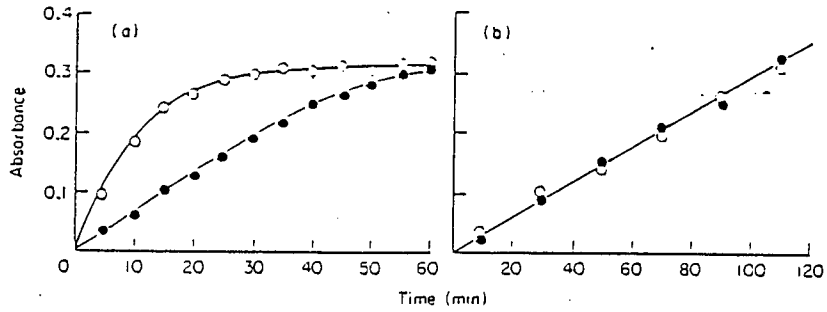

Figure 6. Plots of the absorbance at 300 nm against time for the monomerisation of (○) dimer A and (●) dimer B, by (a) heat at 358 K and (b) photolysis using 254-nm radiation.

when photolysed with radiation of 254 nm wavelength, is illustrated by the plots shown in Figure 6. Attempts to obtain corresponding plots to those of Figure 6a in acidic aqueous solution were unsuccessful because of the rapid conversion of dimer to monomer under acidic conditions. The plot of Figure 6b shows that the photo-reversal is dependent only upon the amount of radiation absorbed; this kind of zero-order behaviour is common for photochemical reactions of this type. T.l.c. of the products after heating or photolysis confirmed that the photo-dimers had been converted to the pyrimidinol I.

The foregoing results on the degradation of the dimers could partly explain why dimers are not formed when compounds such as dimethirimol and ethirimol are exposed to sunlight under natural conditions. Certainly, if dimers were formed in acidic conditions, they would revert rapidly to the parent pyrimidinol. However, it is likely that oxygen plays the most significant role in preventing dimer formation in the environment. It is well known that oxygen acts as an efficient quencher of triplet-state species, and if the major pathway for the formation of dimers is via reaction of the triplet-state pyrimidinol with ground-state pyrimidinol, then the presence of oxygen will prevent the occurrence of this reaction. It is to be noted in this respect that the formation of dimers in the photolysis of thymine is quenched by oxygen.[12]

At high concentrations of a pyrimidinol, aggregates will have an important role in dimer formation, and dimers may be formed when aggregates are photo-excited into their singlet-like manifold. In this situation, oxygen could well prevent dimer formation by reacting chemically with excited singlet-state molecules. This is supported by the fact that oxidation products are formed when ethirimol is photolysed in the presence of oxygen[14] and by the fact that many photo-oxidations of organic compounds occur by direct reaction of singlet-state species with oxygen. Thus, in summary, it is quite possible that dimers are not formed from compounds I–III under natural conditions because of the competitive reaction of oxygen for the photo-excited singlet and triplet-state molecules of the parent pyrimidinols.

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Synthesis of 2,4,8- and 4,5,8- trinitro- and 2,4,5,7- and 2,4,5,8-tetranitro-1-methylnaphthalene

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2,4,6-Trinitrotoluene (TNT) is of well-known importance as a military explosive, but it is of additional importance in that it can be converted readily by the action of base into 2,2',4,4',6,6'-hexanitrostilbene (HNS);[1-3] HNS is used as a crystal modifying additive in melt-cast TNT charges and also as a thermally stable explosive having applications in space technology.[4,5] The ready conversion of TNT into HNS under the influence of base occurs because of the acidity of the methyl protons of TNT induced by the nitro group substituents. In view of the ease with which the methyl group in TNT undergoes coupling, the authors have investigated the nitration of 4,5-dinitro- and 4,8-dinitro-1-methylnaphthalene with a view to obtaining naphthalenic compounds possessing a methyl group susceptible to base-induced coupling. Previous work on the nitration of methylnaphthalenes dealt with the synthesis of mono-[6] and dinitro-1-methylnaphthalenes[7] and only the formation of one tri-nitro derivative, viz 2,4,5-trinitro-1-methylnaphthalene, was reported.[7] As the more highly nitrated compounds are of the greatest interest with respect to coupling reactions of the methyl group, the present authors were principally concerned with the synthesis of tri- and tetra-nitro-1-methylnaphthalenes.

Nitration of 1-methylnaphthalene (I) with dilute nitric acid in 1,2-dichloroethane yielded 4,8-dinitro-(II) and 4,5-dinitro-(III) 1-methylnaphthalene. Subsequent nitration of compounds (II) and (III) gave the desired tri- and tetranitro derivatives. Thus, the reaction of fuming nitric acid with compound (II) in sulphuric acid yielded the new compounds 2,4,8-trinitro-(IV), 4,5,8-trinitro-(V) and 2,4,5,8-tetranitro-1-methylnaphthalene (VI), whereas the action of fuming nitric acid on compound (III) in sulphuric acid resulted in the formation of a new compound, 2,4,5,7-tetranitro-1-methylnaphthalene (VII). Experimental details are as follows.

Preparation of compounds (II) and (III)

Compound (I) (20cm³) was added to 30cm³ of a 2:1 nitric acid (d=1.42):water mixture and the whole was stirred at room temperature for 24h. The deposited solid was filtered off and dissolved in a minimum quantity of 1,2-dichloroethane. To this solution was added nitric acid (d=1.42) (35cm³) and the reactant mixture was stirred vigorously at 40°C for 24h. The organic layer was separated off, washed sequentially with distilled water, sodium hydrogen carbonate solution and finally distilled water prior to being rotary evaporated to give a deep-orange residue. The residue was deposited on silica gel from an acetone solution by rotary evaporation and the coated silica gel applied to the top of a column of dry silica gel (Merck Kieselgel 60, 70-230 mesh, F_{254}). The column was developed using a 4:3 mixture of 1,2-dichloroethane:light petroleum (bp 40-60°C). Five bands were obtained, labelled A-E in decreasing order of R_f value. Band B was extracted into acetone and rechromatographed using a 1:2 mixture of ethyl acetate:light petroleum (bp 40-60°C) to give three bands which were extracted and shown to be (in decreasing order of R_f) 4,8-dinitro-1-methylnaphthalene (II), 2,4-dinitro-1-methylnaphthalene (VIII) and an unidentified dinitro-1-methylnaphthalene. Band C was rechromatographed using the same solvent mixture as for band B and one major band was observed which, on extraction into acetone and evaporation to dryness, yielded 4,5-dinitro-1-methylnaphthalene (III).

Preparation of compounds (IV), (V) and (VI)

Compound (II) (0.3g) was dissolved in 60cm³ of sulphuric acid (d=1.84) maintained at 2°C and to the stirred solution was added a solution of nitric acid (d=1.5) (2cm³) in sulphuric acid (d=1.84) (10cm³) at a rate such that the temperature did not exceed 2°C. After the addition the mixture was

stirred in an ice-bath for 1h, after which time the mixture was poured onto ice and the precipitated solid filtered off, washed thoroughly with water and dried *in vacuo*. The residue was subjected to dry-column chromatography as before, using a 4:3 mixture of 1,2-dichloroethane:light petroleum (bp 40-60°C) as the developing solvent system to yield three principal bands. Extraction of the band of highest R_f value into acetone and subsequent evaporation to dryness yielded compound (IV) (75mg), mp 135-8°C; n.m.r. spectrum (DMSO-d_6), δ 2.51 (3H,*s*), 7.99-8.66 (3H,*m*), 8.91 (1H,*s*); mass spectrum *m/e* 277 (M^+),259 (base peak). Extraction of the band of intermediate R_f value into acetone and subsequent evaporation to dryness yielded compound (V)(40mg), mp 218°C (decomp.); n.m.r. spectrum (DMSO-d_6), δ 2.60 (3H,*s*), 7.95 and 8.65 (2H, ABq, J_{AB}=9.0Hz), 8.43 and 8.65 (2H, ABq, J_{AB}=9.0Hz); mass spectrum *m/e* 277 (M^+), 231 (base peak). The base peak corresponding to $M - NO_2]^+$ showed the existence of *peri*-nitro groups in the compound structure.[9] Extraction of the band of lowest R_f value into acetone and subsequent evaporation to dryness yielded compound (VI) (19mg), mp 220°C (decomp.); n.m.r. spectrum (DMSO-d_6), δ 2.57 (3H,*s*), 8.64 and 8.84 (2H, ABq, J_{AB}=9.0Hz), 9.10 (1H,*s*); mass spectrum *m/e* 322 (M^+), 276 (base peak).

Preparation of compound (VI)

To a solution of compound (III) (0.36g) in sulphuric acid (d=1.84) (60cm³) maintained at −1°C was added a solution containing 2cm³ of nitric acid (d=1.5) in 10cm³ sulphuric acid (d=1.84) at a rate such that the temperature of the reactant mixture was kept close to 0°C. After the addition, the mixture was stirred for 2.5h in an ice-bath, poured onto ice and the precipitated solid washed thoroughly with water and dried *in vacuo*. The residue was subjected to dry-column chromatography as before using a 1:2 mixture of ethyl acetate:light petroleum (bp 40-60°C) as the developing system to yield two main bands. The band of lower R_f value corresponded to a previously reported compound, 2,4,5-trinitro-1-methylnaphthalene.[7] The band of higher R_f value was extracted into acetone and evaporated to dryness to give compound (VII) (21mg), mp 190°C (decomp.); n.m.r. spectrum (DMSO-d_6), δ 3.05 (3H,*s*), 9.12 (1H,*s*), 9.22 and 9.59 (2H, ABq, J_{AB}=3.0Hz); mass spectrum *m/e* 322 (M^+), 276 (base peak).

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C H J Wells

Storing the sun's energy in chemical bonds

The depletion of the fossil fuel resources of the world is of great concern, and has stimulated research into alternative ways of obtaining and storing energy. The sun is the most important energy source for our planet and if the energy of the sun could be harnessed and stored for use by man as a replacement fuel then problems relating to fossil fuels would no longer exist. The sun is a vast energy source for our planet, and in the course of a year the surface of the earth receives 3×10^{24} J of energy, comparable with the estimated proven reserves of natural gas, coal, oil and uranium amounting to 2.5×10^{22} J of energy. Thus, in less than one week the earth receives from the sun an amount of energy equal to the total known reserves.

The most common method to date of storing the sun's energy is the use of solar panels for water heating, but the disadvantage of this method is that the energy absorbed is converted directly into heat or electricity, neither of which can be stored as such.

In recent years interest has been aroused in using photochemical reactions undergone by organic molcules as a means of storing energy. The principle of the method can be illustrated by reference to the photo-isomerisation of norbornadiene (NBD) to quadricyclane (Q) as shown in Scheme 1.

The photo-isomerisation of NBD to Q has energy storage capacity because of bond strain in the product molecule. The energy stored in Q can be released, when desired, by conversion of Q back to NBD, either by the use of a catalyst or by heating. The enthalpy, ΔH, of isomerisation of NBD to Q in the liquid phase is 111 kJ mol^{-1}, and as Q has a molecular weight of 92 the energy storage capacity in Q is equal to 1207 J per gram of material. The potential for energy storage in strained organic molecules becomes evident on comparison of this value with that of water (200 J g^{-1} for a temperature rise of 50 °C) and that of rocks (40 J g^{-1}). Obviously, in order to achieve this potential it is necessary to have as much bond strain as possible in the storage molecule and for this molecule to be of low molecular weight.

The steps in the harvesting of solar energy and in the subsequent storage and release of energy are depicted in *Fig. 1*. In the initial step, solar radiation $h\nu$ is absorbed by the fuel molecule *F* to form an electronically excited species *F** with excess vibrational energy. The excess vibrational energy is rapidly lost and an excited state species *F** in the lowest vibrational level formed. It is this energetically rich species, either in the form of a singlet or triplet state, which isomerises to the storage molecule S and in so doing locks in an amount of energy ΔH. If *S* is a stable entity then the energy ΔH is stored until such time as *S* is heated or subjected to a catalyst in order to promote the reverse reaction $S \rightarrow F$. This reaction has an activation energy, E_A, and occurs via the transition state *T*. Energy is released in the final step and the fuel molecule *F* so regenerated can participate in another cycle of energy absorption, storage and release.

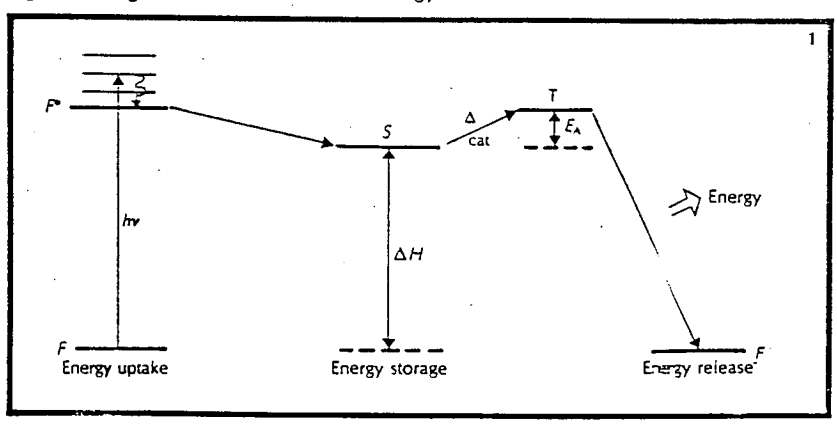
There are a number of criteria relating to the cycle which have to be met to achieve an efficient photochemical storage system.

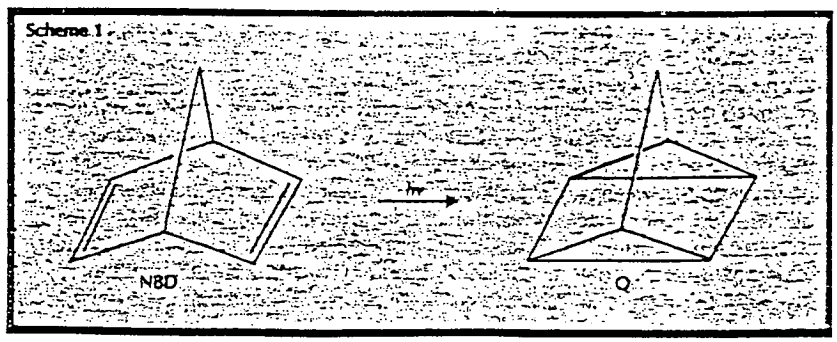
- The fuel molecule *F* should absorb as much sunlight as possible, *ie* the molecule should have high absorption over the wavelength range 300—700 nm.
- The photochemical conversion $F \rightarrow S$ should be efficient, *ie* have a high quantum yield.
- The storage molecule *S* should not competitively absorb sunlight and be converted back to *F*.
- The molecule *S* should have a high energy storage capacity, and yet be thermally stable over long periods of time at room temperature or just above. There are obvious economic advantages in the amount of energy stored, ΔH, being as high as possible, but if ΔH is too high then the activation energy barrier, E_A, between the storage molecule *S* and the fuel molecule *F* will be lower, with a consequent increase in the likelihood of a significant conversion of *S* into *F* occurring at room temperature. In other words, if ΔH is very high the long term thermal stability of *S* may be reduced.
- The chemical yield in each step of the cycle should be high, otherwise side products or degradation products will build up on repeated cycling.

Ideally the material used to fuel a photochemical energy storage system would be an industrial chemical in current production which is cheap and non-hazardous. However, the number of industrial chemicals capable of undergoing energy storing photo-reactions is small and principally limited to the reactions in Scheme 2.

Dicyclopentadiene *1*) is obtained in

Fig. 1. Storage and release of solar energy.





large quantities in the thermal cracking of gas oil and naphtha, 1,5-cyclo-octadiene (2) is readily produced from butadiene which is widely used in the synthetic rubber industry, and limonene (3) is a waste product of the citrus fruit industry. The products of the above photo-reactions have an energy storage capacity approximating to 500 J g^{-1}, and although relatively high the storage capacities are well below that of the NBD/Q system mentioned previously.

The NBD/Q system

The NBD/Q system is one of the most attractive energy storage reactions investigated to date, not only because of the high storage capacity but also because (*i*) Q is extremely stable, (*ii*) both NBD and Q are liquids and are easy to handle, (*iii*) NBD can be manufactured from dicyclopentadiene and acetylene, (*iv*) the photochemical and chemical yields in the forward and reverse reactions of the system are quantitative, and (*v*) the transformation of Q into NBD can be readily catalysed.

The main disadvantage to the use of NBD as a photochemical fuel is that NBD does not absorb in the wavelength range of sunlight. However, this problem in a potential photochemical energy converter can be overcome by the use of sensitisers which absorb sunlight and then transfer the absorbed energy to the fuel molecule; the transfer of absorbed energy from one molecular species to another is a common occurrence in photochemical systems. The process of energy transfer can be represented in simplified form as follows:

Sensitiser + $h\nu \rightarrow$ (Sensitiser)*

(Sensitiser)* + $F \rightarrow$ Sensitiser + F^*

*represents an energetically rich species.

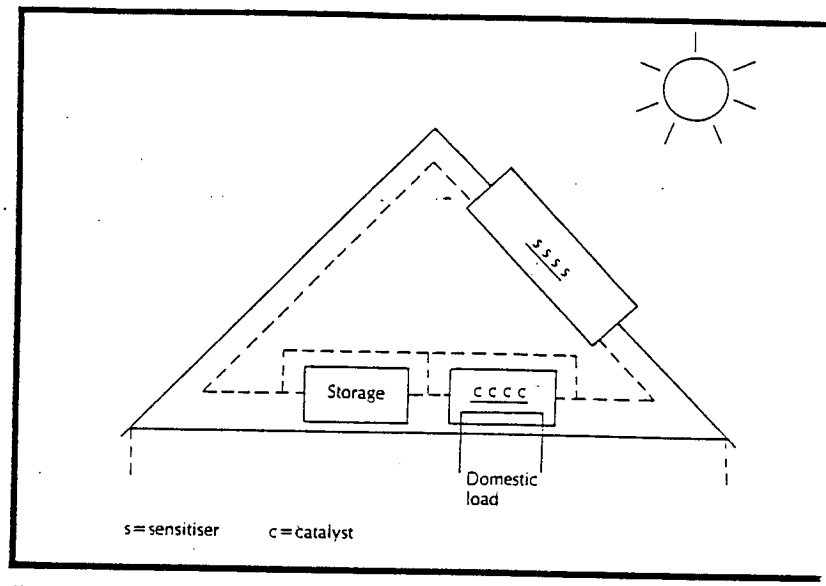


Fig. 2. A possible photochemical solar energy converter.

A possible design for a photochemical solar energy converter is shown schematically in *Fig. 2*. The photochemical fuel *F* would be pumpe round the system and as it passed ove the sensitiser bed, comprising sensitise bound to inert support material, energ transfer would occur from the sensitise to *F* with formation of *F** and consequent conversion of a percentag of the fuel *F* to storage material *S*. The fluid mixture would then flow over a suitable catalyst bed where thermal energy, ΔH, would be released. If the catalyst chamber formed part of a hea exchanger incorporated in a domestic hot water system then the thermal energy released would be available fo household use.

An important advantage of a photochemical solar energy converter is that it is possible to collect solar energ throughout daylight hours and to store the energy continuously in material *S*; the greater the total amount of energy collected so the higher the percentage of *S* in the fluid mixture. The stored energy can then be released, when desired, either during the day or at night. The capacity to store solar energy is an attractive feature of an energy converter system, but whether photochemical devices will come into common usage in the future depends upon the costs and efficiencies of such systems relative to those of conventional solar devices. However, considerable research effort is being expended in the search for efficient low-cost photochemical energy storage systems that will replace solar energy converters.

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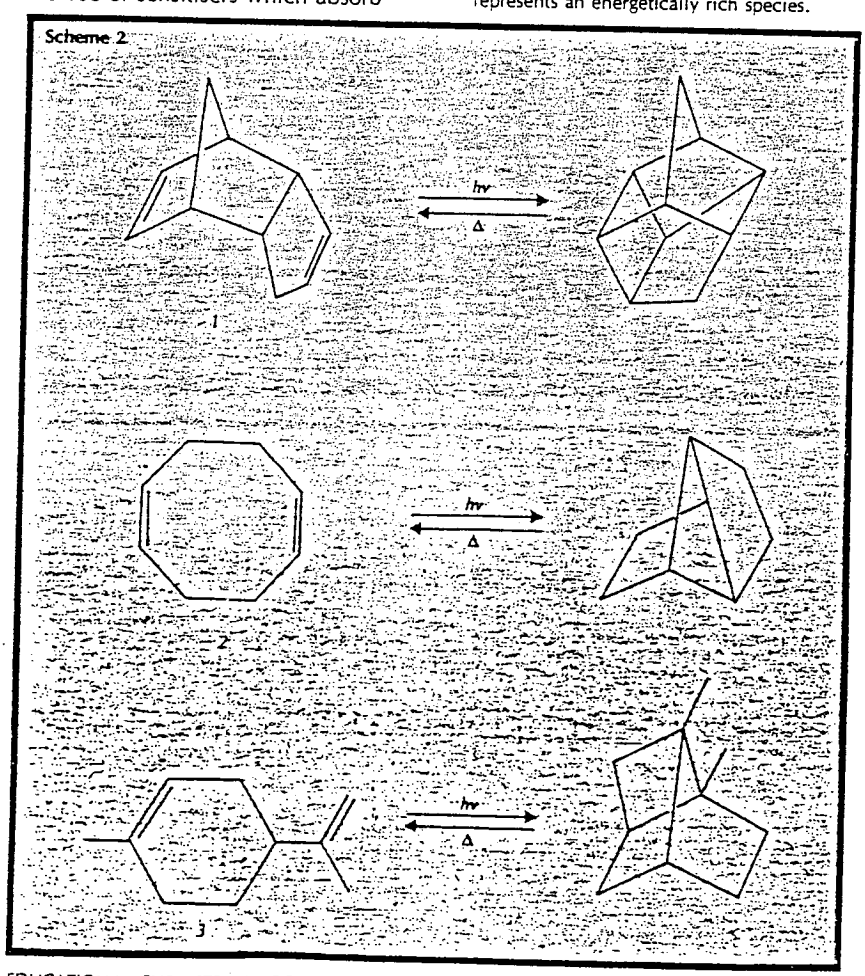
Scheme 2



Barriers to Rotation of the Dimethylamino Group in Some 2-Amino-4-(*N,N*-dimethylamino)pyrimidines

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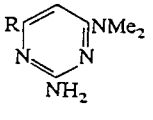
The free energy of activation for rotation about the exocyclic C—N bond of the dimethylamino group of some 6-substituted 2-amino-4-(*N,N*-dimethylamino)pyrimidines has been determined using ^{1}H NMR line shape analysis. The results are discussed in terms of the relative electron-withdrawing and electron-releasing effects of the substituents.

INTRODUCTION

Hindered internal rotation about partial double bonds has been the subject of a great deal of research. The partial double bond character of exocyclic C—N bonds has been of particular interest, and a number of reports have appeared on the barriers to rotation of the C—N bond in *N,N*-dimethylamino-substituted benzenes, pyrimidines and related compounds.[1–5] The thermodynamic parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ relating to rotation about the C—N bond can be determined by line shape analysis of the variable temperature ^{1}H NMR spectra of the *N,N*-dimethylamino group. This method has now been applied to the spectra of the 6-substituted 2-amino-4-(*N,N*-dimethylamino)pyrimidines **1–6** in order to investigate the effect of *meta* substitution on rotation around the C—N bond of the dimethylamino group.



1 R = CH_3 **2** R = $(CH_3)_2CH$ **3** R = Cl
4 R = OH **5** R = NH_2 **6** R = $(CH_3)_2N$

RESULTS AND DISCUSSION

The thermodynamic parameters for hindered rotation about the exocyclic C—N bond of the *N,N*-dimethylamino group in compounds **1–6** are given in Table 1, together with the temperatures, T_c, at which the peaks for the methyl resonances of the *N,N*-dimethylamino group coalesce. The coalescence temperatures for **1–5** span a range of about 100 K and, as expected, the enthalpy of activation, $\Delta H^{\neq}$, decreases as the coalescence temperature falls. Barriers to rotation are best discussed, however, in relation to $\Delta G^{\neq}$ rather than to $\Delta H^{\neq}$ values.[6–9] The values for the free energy of activation at the coalescence temperature, $\Delta G_{T_c}^{\neq}$, (Table 1) are similar in magnitude to those reported[5] for rotation about the exocyclic C—N bond in 2-substituted 4-(*N,N*-dimethylamino)pyrimidines. The results given in Table 1 for **4** show that there is no significant solvent influence on $\Delta G_{T_c}^{\neq}$, in accord with previous findings.[5]

Table 1. Thermodynamic parameters[a] for the barrier to rotation of the dimethylamino group in 4-(*N,N*-dimethylamino)pyrimidines

Compound	Solvent	T_c (K)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta G_{T_c}^{\neq}$ (kJ mol^{-1})
1	$CDCl_3$	276±0.5	75.2±3.5	50±6	61.4
2	$CDCl_3$	283±0.5	78.0±3.9	55±7	62.5
3	$CDCl_3$	243±1	44.8±1.8	−33±3	52.8
4	$CDCl_3$	230±2	41.6±2.6	−48±5	52.7
	CD_3OD	231±1	43.5±1.9	−42±5	53.1
5	CD_3OD	190±3	23.3±0.9	−153±16	52.3
6	CD_3OD	<183			

[a] Errors are the standard deviations from the least-squares plot.

The most notable feature of the results is that the values of $\Delta G_{T_c}^{\neq}$ for **3–5** are constant at approximately 52 kJ mol^{-1}. These compounds have substituents at the 6-position which possess lone-pair electrons, and the values for $\Delta G_{T_c}^{\neq}$ are significantly lower than those for **1** and **2**, in which the substituents at the 6-position do not have lone-pair electrons. The Hammett substituent constants, σ_m, for the Cl, OH and NH_2 groups in **3–5** cover a wide range, being 0.37, 0.12 and −0.016, respectively, and if the bond order of the exocyclic C—N bond at the 4-position was affected by the electron-withdrawing power of the substituent, as has been found for substituents at the 2-position in other 4-(*N,N*-dimethylamino)pyrimidines,[5] then a variation in the $\Delta G_{T_c}^{\neq}$ values for **3–5** would probably have been observable. The relative constancy of the $\Delta G_{T_c}^{\neq}$ values for **3–5** thus suggests that the mesomeric effect of the lone-pair electrons on the substituents outweighs their electron-withdrawing effect.

The canonical forms contributing to the resonance interaction of the *N,N*-dimethylamino group with the ring system can be represented by structures A–C.

The 4- and 6-positions in A–C are equivalent in that both are *ortho* and *para* to the ring nitrogen atoms. When both the substituent, R, at the 6-position and that at the 4-position possess lone-pair electrons, there

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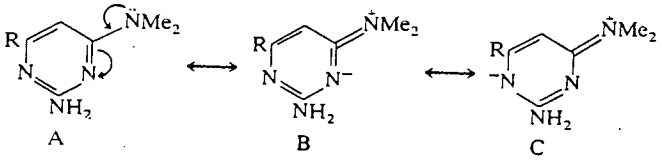

A B C

will be 'competition' between the two substituents in relation to the placement of negative charge at the ring nitrogen atoms. The net result would be that the contribution to the resonance hybrid from structures B and C would be reduced, with a consequent decrease in the bond order of the exocyclic C—N bond at the 4-position. This would be manifested by lower $\Delta G_{T_c}^{\neq}$ values for compounds having substituents with lone-pair electrons at the 6-position compared with compounds having substituents without lone-pair electrons at the 6-position. Thus, it would be expected that **1** and **2**, with alkyl groups at the 6-position, would have higher $\Delta G_{T_c}^{\neq}$ values for rotation about the C—N bond at the 4-position.

The rotational barrier in **6** could not be measured because the coalescence temperature is too low. This was also found for the related compound 2,4,6-tri(*N*,*N*-dimethylamino)pyrimidine.[5]

EXPERIMENTAL

Compounds **1–6** were prepared by refluxing the appropriate 6-substituted derivative of 2-amino-4-chloropyrimidine with a 20 fold molar excess of dimethylamine in propan-1-ol for 2–3 h, evaporating the reaction mixture to dryness under reduced pressure and recrystallizing the residual solid from either toluene, toluene–ethanol (95:5) or benzene–toluene (95:5). The compounds were characterized by NMR and mass spectral data.

The NMR spectra were recorded on a Perkin–Elmer R32 90 MHz spectrometer. The rate constants for rotation about the C—N bond of the *N*,*N*-dimethylamino group were determined by the standard method of line shape analysis using the equations of Gutowsky and Holm and assuming equal population of sites.[10] The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained using absolute rate theory.

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Dye-sensitised Photo-oxidation of 2-Dimethylamino-5,6-dimethylpyrimidin-4-ol in Aqueous Solution

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The sensitisation by Rose Bengal of the photo-oxidation of 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (I) has been studied in aqueous solution by monitoring the rate of oxygen consumption in the system. The results are in accord with a mechanism whereby I is oxidised via a reaction with singlet oxygen. Values for the rate constant for the reaction of I with singlet oxygen have been determined over the temperature range 279–296 K, and the energy of activation and entropy of activation for the reaction have been evaluated as 71.9 kJ mol^{-1} and 150.5 J K^{-1} mol^{-1}, respectively. The positive value for the entropy of activation suggests that the reaction intermediate could have a zwitterionic form. The effect of pH on the reaction rate has been investigated, and the increased rate at high pH has been attributed to an increase in singlet oxygen production as the pH is raised.

1. Introduction

Pyrimidine bases play an important role in agricultural chemistry, and compounds such as ethirimol (5-butyl-2-ethylamino-6-methylpyrimidin-4-ol) and dimethirimol (5-butyl-2-dimethylamino-6-methylpyrimidin-4-ol) are used as systemic fungicides, whilst pirimicarb (2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate) is used as an insecticide. Pirimicarb can be readily hydrolysed to 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (I) (ICI Ltd., Plant Protection Division; private communication); consequently, I may be formed in the environment and subsequently react photochemically.

The ground state of oxygen is a triplet state having two unpaired electrons, but on transfer of absorbed photon energy to oxygen, an electronically excited singlet state of oxygen can be produced in which all the electrons are paired. The singlet oxygen so formed is a highly reactive electrophile,[1] and the oxidation of chemical species by reaction with singlet oxygen is a possible mode of environmental degradation.[2] It is noteworthy in this respect that singlet oxygen has been detected in natural surface waters and shown to act as an oxidising agent in this environment.[3,4] As dyes can act as efficient energy transfer agents for the production of singlet oxygen,[1] a study has been undertaken of the dye-sensitised photo-oxidation of I in aqueous solution in order to ascertain whether the reaction with singlet oxygen could provide a possible route for the environmental degradation of I. The ability of singlet oxygen to react in chloroform solution with I and a number of structurally related compounds has been demonstrated previously.[5]

2. Experimental methods

Compound I was prepared by the method described previously.[6] Rose Bengal (Colour Index 45440) (Aldrich Chemical Co. Inc.) and sodium azide (Hopkin and Williams Ltd) were used as supplied. Solutions containing Rose Bengal (20 μmol) and various concentrations of I in water were placed in the sample compartment of an oxygen electrode (Rank Bros., Bottisham, Cambridge), and the space above the sample solution was filled with nitrogen. The solutions were photolysed

in a dark box using light from a microscope lamp. The light from the lamp was filtered through a Kodak Wratten gelatin filter which absorbed radiation of all wavelengths less than 420 nm. The rate of oxygen removal was monitored using a precalibrated chart recorder and all the rates were measured in quadruplicate. In the experiments using sodium azide as a quencher, solutions containing Rose Bengal (20 μmol), compound I (0.1 mmol) and various concentrations of sodium azide (0–10 mmol) in water were placed in Pyrex glass vessels and simultaneously exposed to sunlight for a period of time such that, in the solutions without sodium azide, the consumption of I was approximately 50%. The amount of I that had reacted in each solution was determined by measuring the absorbance of the solution at 277 nm before and after photolysis.

3. Results and discussion

Production of singlet oxygen ($^1O_2$) via energy transfer from a dye photosensitiser involves the following processes:[1]

$$\text{Dye}\,(S_0) \xrightarrow{I_a} \text{Dye}\,(S_1) \tag{1}$$

$$\text{Dye}\,(S_1) \xrightarrow{k_F} \text{Dye}\,(S_0) + h\nu \tag{2}$$

$$\text{Dye}\,(S_1) \xrightarrow{k_{IC}} \text{Dye}\,(S_0) \tag{3}$$

$$\text{Dye}\,(S_1) \xrightarrow{k_{ISC}} \text{Dye}\,(T_1) \tag{4}$$

$$\text{Dye}\,(T_1) \xrightarrow{k_d} \text{Dye}\,(S_0) \tag{5}$$

$$\text{Dye}\,(T_1) + {}^3O_2 \xrightarrow{k_{O_2}} \text{Dye}\,(S_0) + {}^1O_2 \tag{6}$$

where I_a represents the intensity of absorbed radiation; S_0, S_1 and T_1 represent, respectively, the ground state, first excited singlet state and lowest triplet state of the dye molecule; k_F, k_{IC} and k_{ISC} represent, respectively, the rate constants for fluorescence, internal conversion and intersystem crossing from the S_1 state; k_d is the rate constant for intersystem crossing from the T_1 state of the dye; k_{O_2} represents the rate constant for the process whereby energy is transferred, from the electronically excited dye in its T_1 state, to molecular oxygen in its ground state, to give the dye in its original S_0 state and the electronically excited form of oxygen $^1O_2$.

If a pyrimidine species (Pyr) that reacts with singlet oxygen is present, then the following reactions have to be included in the overall reaction mechanism:

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \tag{7}$$

$$^1O_2 + \text{Pyr} \xrightarrow{k_r} \text{Products} \tag{8}$$

Application of the steady state principle, to the reaction sequence given by Equations 1 to 8 results in the following expression:[7]

$$[-\mathrm{d}(O_2)/\mathrm{d}t]^{-1} = (1/I_a\Phi_T) + (1/I_a\Phi_T) \times (k_d/k_r) \times (1/[\text{Pyr}]) \tag{9}$$

where $\Phi_T = k_{ISC}/(k_F + k_{IC} + k_{ISC})$.

If the above mechanism represents that for the dye-sensitised photo-oxidation of I, then a plot according to Equation 9 of the reciprocal of the rate of oxygen removal, versus the inverse of the concentration of pyrimidin-4-ol, should yield a straight line. Furthermore, the ratio of slope/intercept for the plot will be equal to k_d/k_r, and as k_d is known to have a value of 5×10^5 s^{-1} in aqueous solution,[8] the value of k_r can be determined. Plots according to Equation 9 are shown in Figure 1, and the linearity of the plots is consistent with the mechanism given above for the photo-

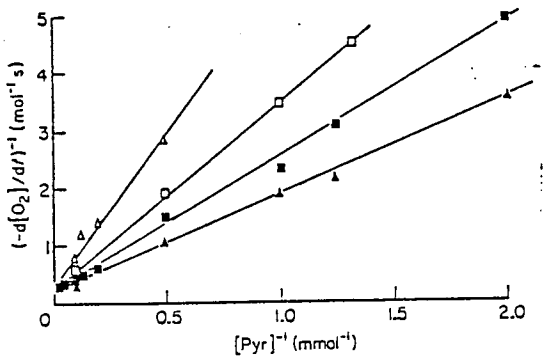

Figure 1. Plots according to Equation 9 for the photo-oxidation of compound I in aqueous solution at: (△) 279 K; (□) 285 K; (■) 289 K and (△) 296 K.

oxidation of I, when sensitised by Rose Bengal. The involvement of singlet oxygen in the reaction mechanism is supported by comparison of the rates of reaction when water (H_2O) was used as solvent to those when deuterium oxide (D_2O) was used as solvent (see Table 1). It can be seen from Table 1 that the rate of reaction was increased from six- to eight-fold over a pyrimidin-4-ol concentration range of 0.5–2.0 mmol, when D_2O was used as the solvent. This arises because the lifetime of singlet oxygen is significantly greater in D_2O than in H_2O;[7–9] consequently, as the steady-state concentration of singlet oxygen was higher in the deuteriated solvent, the rate of reaction was also higher.

The solvent isotope effect will only manifest itself when $k_d \gg k_r$ [Pyr], and at relatively high values of [Pyr] the effect will become less apparent. This is seen in the results given in Table 1 which shows that the ratio of the rate of reaction in D_2O to that in H_2O dropped markedly as the concentration of I was increased above 2 mmol. The difference in rate between the deuteriated and non-deuteriated systems could conceivably have been due to a difference between Φ_T in these

Table 1. Rate of oxygen consumption (R) in water (H_2O) and deuterium oxide (D_2O) at 289 K

[Pyr] (mmol)	10^7 $R(H_2O)$ (mol dm^{-3} s^{-1})	10^7 $R(D_2O)$ (mol dm^{-3} s^{-1})	$R(D_2O)/R(H_2O)$
0.5	0.21	1.65	7.85
0.75	0.29	2.26	7.75
1.0	0.45	3.04	6.75
2.0	0.67	4.51	6.73
5.0	1.65	4.83	2.93
25.0	3.20	4.16	1.30

systems, and this has to be borne in mind when interpreting the differences in rate brought about by a solvent isotope effect. The involvement of singlet oxygen in the reaction was confirmed, however, by the observation that sodium azide, a known singlet oxygen quencher,[11,12] inhibits the reaction. This is seen from the results given in Table 2 which show that for the solutions containing sodium azide, the extent of the reaction, relative to the unquenched reaction, decreased as the concentration of the quencher was increased.

Values for the rate constants (k_r) for the reaction of I with singlet oxygen over the temperature range 279–296 K are summarised in Table 3. These values give a linear Arrhenius plot from which the energy of activation for the reaction is evaluated at 71.9 kJ mol^{-1}. The experimental data also yield a value of 150.5 J K^{-1} mol^{-1} for the entropy of activation.

Table 2. Effect of sodium azide, a known quencher (Q) of singlet oxygen, on the extent of the reaction

[Q] (mmol)	Δ_Q/Δ_0[a]
0.0	1.0
0.1	0.99
0.5	0.96
1.0	0.74
5.0	0.47
10.0	0.29

[a] Δ_Q is the decrease in absorbance at 277 nm in the presence of the quencher; Δ_0 is the decrease in absorbance in the absence of the quencher.

Table 3. Rate constants (k_r) for the reaction of compound I with singlet oxygen, as determined from plots shown in Figure 1

Temperature (K)	$10^{-7}\ k_r$ ($dm^3\ mol^{-1}\ s^{-1}$)[a]
279	1.52 (±0.16)
285	2.91 (±0.19)
289	4.47 (±0.11)
296	8.99 (±0.12)

[a] Errors are the standard deviations from the least-squares plot.

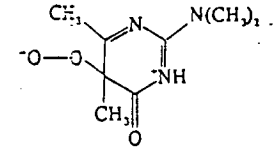

Figure 2. Possible zwitterionic intermediate in the reaction of singlet oxygen with compound I.

Previous studies[5] on the reaction of singlet oxygen with I and other structurally related pyrimidin-4-ols indicated that the site of attack by singlet oxygen is at the 5,6-double bond of the parent pyrimidine. This, combined with the large positive value now determined for the entropy of activation, suggests that the transition state could well have the zwitterionic structure shown in Figure 2. Zwitterions have been postulated as intermediates in a number of reaction systems involving singlet oxygen reacting with heterocyclic compounds.[13–15] The positive entropy of activation for the reaction of I with singlet oxygen is in contrast with the negative values that have been reported for the reaction of singlet oxygen with other olefinic systems.[16,17]

Measurements on the rate of reaction of singlet oxygen with I over a range of pH values resulted in straight line plots similar to those of Figure 1. The linearity of the plots at low, intermediate and high pH values indicated that the mechanism of the reaction did not alter as the pH was changed,

Table 4. Effect of pH on the rate constant for the reaction of compound I with singlet oxygen

pH	$10^{-7}\ k_r$ ($dm^3\ mol^{-1}\ s^{-1}$)
4.0	4.35 (±0.86)
7.0	8.07 (±1.98)
9.0	14.14 (±0.61)

and oxygen was removed from the system via the reaction of singlet oxygen with the pyrimidine species, as represented in Equation 8. Values for the rate constant (k_r) of the reaction at different pH values are given in Table 4, from which it can be seen that the rate constant increased as the pH was increased. This could be the result of two factors: a change with pH of the pyrimidinol species present and/or an increase in the steady-state concentration of singlet oxygen as the pH was increased. It has been found[18] that a cationic pyrimidinol species is present at low pH, and an anionic pyrimidinol species at high pH, these species being in equilibrium with the neutral pyrimidinol which is itself the principal species present at intermediate pH. As singlet oxygen is an electrophile, reaction with the anionic form present in alkaline solution would have the highest rate. However, the pK_a value[18] for proton loss from I is such that the concentrations of I at pH 7 and pH 9 are similar, whilst at pH 9, the concentration of I is some ten-fold greater than that of the anionic form. Thus the increase in the value of k_r with pH is most probably due to an increase in the steady-state concentration of singlet oxygen as the pH is raised. This is in accord with previous observations[19,20] that the efficiency of singlet oxygen production, using dye sensitisers, is much greater in a basic medium than in an acidic medium.

4. Conclusions

The dye-sensitised photo-oxidation of I in aqueous solution probably involves singlet oxygen as the reactive intermediate responsible for the initial attack on the substrate. As singlet oxygen can be present in natural surface waters, it is possible that photo-oxidation of I in water under field conditions could occur via a reaction with singlet oxygen, and that the mechanism may be similar to that given herein.

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Substituent Pattern Effect in the Reaction of Dimethyltrinitronaphthalenes with Di- and Triethylamine

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Einfluß der Substituenten-Stellung bei der Reaktion von Dimethyltrinitronaphthalin mit Di- und Triethylamin

Reaktionskinetische Untersuchungen der Reaktion zwischen Di- und Triethylamin und 1,8-Dimethyl-2,4,5-trinitronaphthalin (245 TND) in Dimethylsulfoxid und Dimethylsulfoxid/Methanol Lösungsmittelsystemen wurden ausgeführt, sowie Vergleiche mit Ergebnissen der entsprechenden Reaktionen mit 1,5-Dimethyl-2,4,8-trinitronaphthalin (248 TND) angestellt. Die Ergebnisanalyse zeigt, daß das benzylartige Anion leichter mit 245 TND gebildet wird als mit 248 TND. Also hat 245 TND das höhere Potential für eine durch Basen induzierte Kopplung, um einen hitzebeständigen Sprengstoff zu erhalten.

Influence de la position des substituants dans la réaction des diméthyltrinitronaphthalènes avec la diéthylamine ou la triéthylamine

On a étudié la cinétique de la réaction entre la diéthylamine et la triéthylamine d'une part et le 1,8-diméthyl-2,4,5-trinitronaphthalène (245 TND) d'autre part, en présence d'un solvant constitué soit par du diméthylsulfoxyde, soit par un mélange de diméthylsulfoxyde et de méthanol. Les résultats ont été comparés à ceux obtenus par la réaction correspondante du 1,5-diméthyl-2,4,8-trinitronaphtalène (248 TND). Cette comparaison montre que la formation d'un anion du type benzyle est plus facile à partir due 245 TND qu'à partir du 248 TND. Il apparaît donc que le 245 TND se prête mieux à un couplage en milieu basique pour fournier une substance explosive thermiquement stable.

Summary

The kinetics of the reaction of di- and triethylamine with 1,8-dimethyl-2,4,5-trinitronaphthalene (245 TND) have been studied in dimethylsulfoxide and dimethylsulfoxide-methanol solvent systems and comparison made with data for corresponding reactions involving 1,5-dimethyl-2,4,8-trinitronaphthalene (248 TND). Analysis of the results shows that the formation of a benzyl-type anion is more facile with 245 TND than with 248 TND. Thus, the former compound has the greater potential for base-induced coupling to give thermally stable explosive material.

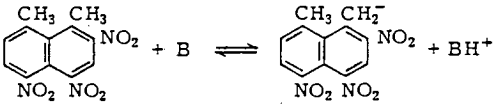
1. Introduction

The action of base on alkyl substituted polynitroaromatic compounds has been the subject of extensive research[1–5] and, in this category, reactions involving 2,4,6-trinitrotoluene (TNT) have been of particular commercial importance because of base-induced coupling to give the thermally stable explosive 2,2′,4,4′,6,6′-hexanitrostilbene[6–10]. The reaction of TNT with the base moiety of certain surfactants is also of importance as a means of removing TNT from wastewater emanating from plants engaged in the production and packaging of this explosive[11]. The reactivity of TNT is associated with the acidity of the methyl group and reaction with base can occur via hydrogen abstraction from the methyl group to give a benzyl-type anion[12–14].

The authors have been concerned with the reaction of base with alkyl substituted polynitronaphthalenic compounds with a view to the preparation of thermally stable explosive materials and have found that a benzyl-type anion is formed in the reaction of 1,5-dimethyl-2,4,8-trinitronaphthalene (248 TND) with methoxide ion[15], and di- and triethylamine[16], and kinetic and equilibrium data for the reaction with di- and triethylamine have been reported[16]. In order to ascertain the effect of the pattern of substituents on the reactivity of the parent alkyl substituted polynitronaphthalene, a study has been undertaken of the kinetics of the reaction of 1,8-dimethyl-2,4,5-trinitronaphthalene (245 TND) with di- and triethylamine in DMSO and DMSO-MeOH solvent systems and comparison made with corresponding data for the reaction with 248 TND.

2. Results and Discussion

The addition of three equivalents of diethylamine to a solution of 245 TND in [$^2H_6$]-DMSO resulted in the following ^1H NMR spectrum assignable to the benzyl-type anion shown in the scheme:



δ 2.60 (3H, s), 5.24 (1H, s), 6.18 (1H, s), 7.26 and 7.59 (2H, AB_q, J_{AB} 8.3 Hz), 8.65 (1H, s). The visible absorption spectrum obtained on diluting a solution which gave the NMR spectrum of the anion showed a single peak with λ_{max} = 558 nm. Similar ^1H NMR and visible absorption spectra were obtained for the product formed when triethylamine was added to 245 TND in [$^2H_6$]-DMSO.

Kinetic results were obtained by monitoring the change with time of the absorbance at 558 nm due to the anion. All measurements were made under first-order conditions with the base concentration in large excess. Second-order rate constants for the forward reaction were obtained from the slope of the plot of pseudo first-order rate constants against base concentration. The second-order rate constant, k, the enthalpy of activation, $\Delta H^{\neq}$, and the entropy of activation, $\Delta S^{\neq}$, for the reaction at 298 K are listed in Table 1. The corresponding values for reaction with 248 TND are also listed for comparison.

The results show that the rate constant, k, for the reaction of 245 TND with both amines increases as the % DMSO in the

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Table 1. Kinetic Parameters for the Reaction of 245 TND with Di- and Triethylamine in DMSO and DMSO-MeOH at 298 K[a]

Base	% DMSO	10^2k[dm³/mol · s]	$\Delta H^{\neq}$[kJ/mol]	$\Delta S^{\neq}$[J/K · mol]
Et_2NH	100	89.4 (42.0)	22.6 ± 3.0 (34.9)	−170 ± 6 (−135)
	67	28.0 (7.89)	37.4 ± 3.0 (45.6)	−130 ± 6 (−113)
Et_3N	100	13.8 (5.50)	31.4 ± 2.5 (45.9)	−156 ± 5 (−115)
	67	5.84 (2.48)	38.6 ± 3.0 (43.7)	−139 ± 6 (−129)

[a] Values in brackets refer to the corresponding reaction[16] with 248 TND.

solvent increases. Also the $\Delta H^{\neq}$ value for the reaction of 245 TND with both amines is lower than for the corresponding reactions with 248 TND implying that it is easier to abstract a proton from the 1-methyl group in 245 TND than in 248 TND. Since steric interaction between the two peri nitro groups in 245 TND twists the groups out of planarity with the aromatic ring system there is likely to be a resultant decrease in the electron withdrawing power relative to that for two planar nitro group substituents[17, 18]. It might be expected, therefore, that the acidity of the methyl protons at the 1-position in 245 TND would be less than that of the corresponding protons in 248 TND, and that the value of $\Delta H^{\neq}$ would be higher in the former system. That this is not the case may well be due to the bulky nitro groups at the 2- and 8-positions in 248 TND sterically hindering hydrogen abstraction from the 1-methyl group by the amines resulting in a higher value of $\Delta H^{\neq}$ for the reaction of 248 TND with both amines.

The entropy of activation, $\Delta S^{\neq}$, is large and negative for the reaction of 245 TND with both amines in both solvent systems, indicating that the activated complex is more highly ordered than are the reactants. Moreover, since $\Delta S^{\neq}$ has a greater negative value for the reaction of 245 TND with the two amines in both solvent systems than for the reaction of 248 TND, it appears that there is a greater restriction in the activated complex formed in the former systems. Shielding of the 1-methyl group in 248 TND by the adjacent nitro groups would cause the degree of bonding in the activated complex between the nitrogen atom of the amine and the hydrogen atom of the methyl group to be less than that for the corresponding complex involving 245 TND. This would give rise to a "less-ordered" complex in the case of 248 TND, and $\Delta S^{\neq}$ for the formation of the complex would be expected to be less negative than for the formation of the complex from 245 TND. The fact that the value of $\Delta S^{\neq}$ for the reaction of 245 TND with diethylamine in 100% DMSO is more negative than the corresponding value for the reaction with triethylamine suggests, as was the case for 248 TND, that the activated complex has an eight-membered ring structure in which there is partial bonding between the hydrogen atom of diethylamine and an oxygen atom of the 2-nitro group[16].

From the above, it is apparent that the pattern of nitro and methyl group substituent in 1-methyl substituted naphthalenes has a marked effect on proton abstraction from the 1-methyl group by di- and triethylamine in DMSO and DMSO-MeOH solvent systems. Interchanging a methyl group and a nitro group between the 5- and 8-positions in going from 248 TND to 245 TND increases the rate of proton abstraction and greatly increases the proportion of benzyl-type anion present at equilibrium. This has obvious implications for the base-induced coupling of alkyl substituted polynitronaphthalenes to give potential thermally stable explosive compounds.

3. Experimental

1,8-Dimethyl-2,4,5-trinitronaphthalene (245 TND) was prepared and purified as previously described[19]. Reagent grade di- and triethylamine were distilled using a Fischer Spaltrohr 60 theoretical plate column, the middle fractions being selected. Dimethylsulfoxide, [$^2H_6$]-dimethylsulfoxide, Analar methanol were dried over molecular sieve prior to use.

NMR spectra were recorded on a Perkin-Elmer R 32 spectrometer. Samples were prepared by adding the appropriate amount of di- and triethylamine to a solution of 245 TND in [$^2H_6$]-dimethylsulfoxide in an NMR tube.

Visible absorption spectra were recorded on a Perkin-Elmer SP 1700 spectrophotometer using 10 mm matched cells in a thermostatted cell compartment maintained at ± 0.1 °C. Reaction mixtures were prepared by mixing thermostatted solutions of 245 TND with the appropriate amine in a cell capped with a PTFE stopper.

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Green – the predominant colour of nature

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Green is the colour man most commonly perceives around him in his natural environment, and the question may be asked as to why man sees the leaves of trees, grass and the foliage of plants as green and not some other colour. The answer lies in the response of the eye and brain to different wavelengths of visible radiation, and in the wavelength range of light reflected from the surface of leaves, grass and foliage.

Visible radiation (white light) is that part of the electromagnetic spectrum with a wavelength range of 400-700 nm. In 1672 Isaac Newton used a prism to demonstrate that white light could be separated into its component colours – violet, indigo, blue, green, yellow, orange and red. The colour of objects most commonly arises because radiation of particular wavelengths is preferentially removed from white light by absorption at the surface of, or within the object. Thus, if radiation of wavelengths corresponding to violet, indigo, blue, yellow, orange and red is preferentially absorbed, then the radiation reflected from the surface of the object will be principally comprised of wavelengths corresponding to the green region of the spectrum.

"Green" is the interpretation by the brain of the effect produced upon the eye by radiation covering the wavelength range 490-575 nm. In the eye there are two kinds of light receptor, viz. rods and cones. Rod cells are sensitive to low levels of light whilst cone cells are sensitive to bright light and colour. There are in fact three types of cone cell, each with a different response to radiation in the visible region. The response curves of the three types of cone cell (blue, green and red) are shown in Figure 1. Almost any colour sensation can be created by combining blue, green and red at different levels of intensity, and colour perception in man is based on the relative extent to which the different receptor cones are stimulated.

The site of light absorption in a plant is the photosynthetic cell and it is here that the energy from sunlight is taken up and converted to stored chemical energy. In a blade of grass, for example, the photosynthesising cells lie just underneath the upper and lower epidermis (Figure 2). The principal light absorbers in the photosynthesising cells of a green plant are chlorophyll a and chlorophyll b, these compounds being con-

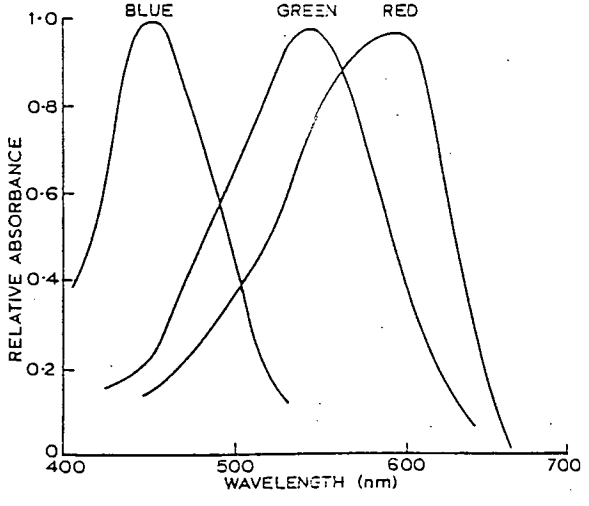

Figure 1. Response curves for the three types of cone cell

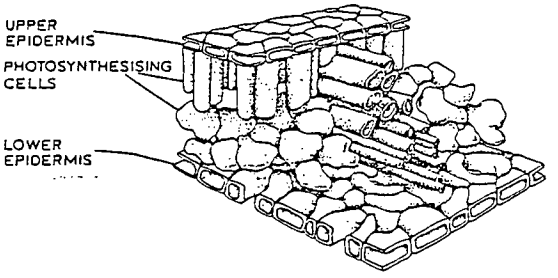

Figure 2. Cut-away section of a blade of grass

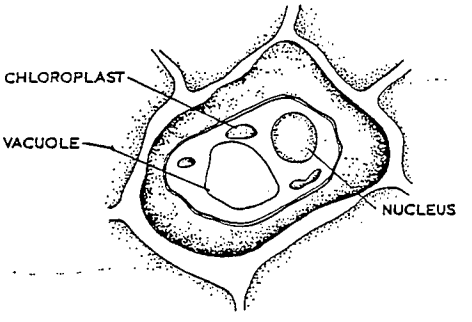

Figure 3. Section of a photosynthesising cell

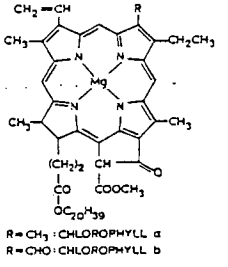

Figure 4. Structures of chlorophyll a and chlorophyll b

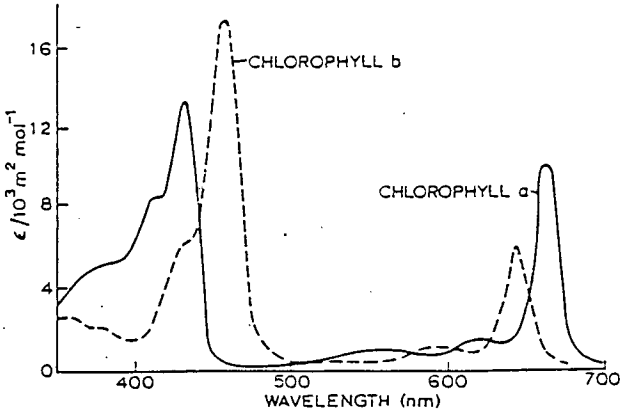

Figure 5. Visible absorption spectra of chlorophyll a and chlorophyll b

tained in the chloroplast of the cell (Figure 3). The chlorophyll content of the chloroplast is some 70 per cent chlorophyll a and 30 per cent chlorophyll b. The structures of chlorophylls a and b are shown in Figure 4 and their absorption spectra in Figure 5. Evidence that the chlorophylls are the major light receptors in the photosynthesising cells of green plants comes from the similarity between their absorption spectra and the action spectrum for photosynthesis (Figure 6). It can be seen from figures 5 and 6 that the chlorophylls absorb most strongly at those wavelengths which are most effective in photosynthesis, viz. the wavelengths corresponding to the blue and red regions of the visible spectrum. Radiation reflected from a substrate in which chlorophyll is the major absorber will be composed mainly of wavelengths spanning the range 490-600 nm. This radiation will stimulate the green receptor cone of the eye preferentially and the substrate will be perceived as being green.

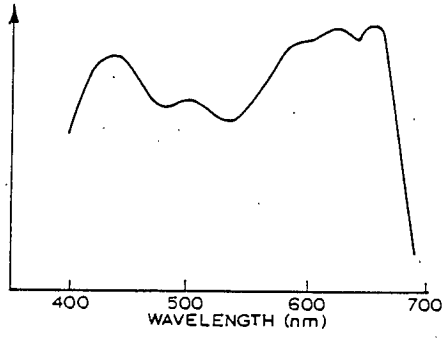

Figure 6. Action spectrum for photosynthesis in a bean leaf

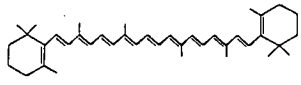

Figure 7. Structure of β-carotene

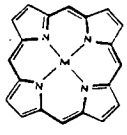

Figure 8. Structure of a metalloporphin showing 16-atom conjugation (heavy-line)

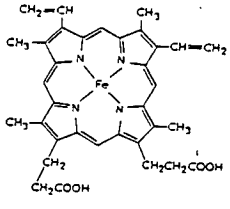

Figure 9. Structure of iron (II) protoporphin

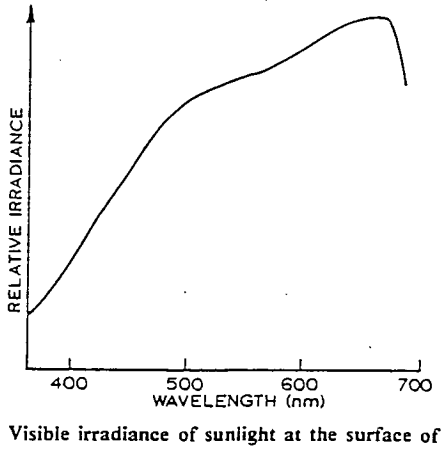

Figure 10. Visible irradiance of sunlight at the surface of the earth

Light absorption in the chloroplast other than by the chlorophylls occurs through the presence of carotenoids such as β-carotene (Figure 7).

Whereas the chlorophylls represent approximately 11 per cent of the total mass of a photosynthesising cell, the carotenoids represent only about 1 per cent of the mass. However, carotenoids absorb in the blue region of the visible spectrum and so their presence supplements the blue absorption of the chlorophylls.

Chlorophylls absorb radiation in the visible because of the extended conjugation which exists within their molecular framework. This is illustrated by the heavy lining in the structure of Figure 8 wherein a 16-atom conjugated pathway in a metalloporphin is traced out. The wavelength of the lowest energy absorption in conjugated systems increases with the extent of conjugation, as exemplified by the series butadiene (180 nm), hexatriene (258 nm) and octatetraene (300 nm). These compounds have two, three and four conjugated bonds respectively and as the number of conjugated bonds increases so the absorption shifts closer to the blue. Thus in β-carotene, where there are 11 conjugated bonds, the longest wavelength absorption falls in the blue region. With the degree of conjugation that exists in chlorophyll it is to be expected that absorption will occur in the visible region. Theoretical calculations, beyond the scope of this review, predict two principal absorption bands in the visible region for the chlorophylls and related structures. For chlorophyll a, one band of moderate intensity (molar absorptivity, $\varepsilon_{max} \approx 8 \times 10^3$ m^2 mol^{-1}) is observed at approximately 670 nm, and the other of higher intensity ($\varepsilon_{max} \approx 16 \times 10^3$ m^2 mol^{-1}) is observed close to 450 nm. These bands are referred to as the Q and B bands respectively.

It is interesting to speculate as to why the predominant photosynthetic pigment in nature is chlorophyll and why, therefore, the predominant colour is green. Why is another metalloporphin such as iron (II) protoporphin (Figure 9) not the major pigment and grass and plant foliage not red as a consequence? This must be, presumably, a question of efficiency through evolutionary history. The spectral irradiance of sunlight falling on the surface of the earth spans the visible region (Figure 10), and the fact that the chlorophylls absorb strongly in both the blue and red regions makes them good harvesters of solar radiation. Thus plants containing chlorophyll are particularly efficient in harnessing the energy of sunlight for use in producing carbohydrate. This means that green plants have the built-in ability to proliferate on the earth's surface relative to plants containing other photosynthetic pigments. In places where the incident radiation is not normal daylight, such as under water where the light is more blue, life using rarer photosynthetic pigments can be more efficient in capturing the available light and organisms coloured red or brown are more commonplace.

In summary, the perception by man of colour as has been outlined above is a result of a series of steps. The process starts with the emission of visible radiation from the sun, some of which will eventually reach the surface of the earth. If this radiation is incident upon an object in which certain wavelengths are preferentially absorbed, then only the non-absorbed radiation will be reflected to the eye of an observer. This reflected radiation will stimulate one or more of the colour cones in the eye and a signal will be sent to the visual cortex of the brain. When the primary light absorber is chlorophyll, the reflected radiation will be principally composed of wavelengths in the range 490-575 nm and the final signal will be registered as green.

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Spectral Problems in Organic Chemistry

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Preface

There have been many advances made in spectroscopy in recent years. One of the most important of these has been the advent of pulsed Fourier Transform n.m.r. spectrometers which enable ^{13}C n.m.r. spectra of organic compounds to be obtained on a routine basis. The increasingly widespread use of such spectrometers has had an impact on the teaching of spectroscopy in relation to structure elucidation, and nowadays as much emphasis is placed on the ^{13}C n.m.r. spectrum of a compound as on its ^{1}H n.m.r. spectrum. It is of importance, therefore, that students be able to interpret the information available in a ^{13}C n.m.r. spectrum. Consequently, we have compiled a set of structural problems in which the ^{13}C n.m.r. spectra of a selection of organic compounds are presented alongside their ^{1}H n.m.r. spectra. In real life, such spectra are used in conjunction with infrared and mass spectra to aid unambiguous structure elucidation. Thus, for each of the problems, the infrared, ^{1}H n.m.r., ^{13}C n.m.r. and mass spectra of the compounds are presented, together with either analytical data or a molecular formula.

The spectral problems are graded in complexity, beginning with those of relative simplicity and ending with what we believe are quite challenging examples. If we have erred towards the side of simplicity in the collection then it is intentional. It is hoped that undergraduate students in their early years at British universities and polytechnics should be able to solve the majority of problems without too much difficulty and so gain experience and confidence in the use of spectral data for the elucidation of organic molecular structures. It is also the intention that the problems should be of value to the teaching of spectral interpretation to undergraduates in other countries.

We should like to thank Mr T. Mills and Mr M. Stephens for assistance in recording the n.m.r. and mass spectra respectively. We should also like to thank Dr A. Cooper for a gift of one of the compounds.

R.D.
C.H.J.W.

Contents

Reactions between Dinuclear Metal Carbonyl Complexes and Alkyl Halides: Formal Oxidative Addition across a Metal–Metal Single Bond

Michael A. Biddulph, Reg Davis,* Clifford H. J. Wells, and Fiona I. C. Wilson

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Photochemical reactions between $[Mn_2(CO)_8(PR_3]_2]$ (R = Et, Bu^n, OEt) and alkyl halides (R'X) proceed to completion in 2 to 4 h yielding equimolar quantities of $[MnR'(CO)_4PR_3]$ and $[MnX(CO)_4PR_3]$, by a route involving reaction of R'X with mononuclear intermediates.

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Photochemical reactions between $[Mn_2(CO)_8(PR_3]_2]$ (R = Et, Bu^n, OEt) and alkyl halides (R'X) proceed to completion in 2 to 4 h yielding equimolar quantities of $[MnR'(CO)_4PR_3]$ and $[MnX(CO)_4PR_3]$, by a route involving reaction of R'X with mononuclear intermediates.

There has been considerable interest in the photochemical reactions of metal–metal bonded dimers of the type $[L_m(OC)_nM–M(CO)_nL_m]$. Until recently most of these processes were believed to proceed by M–M bond homolysis [equation (1)], the reactions, thus, being those of the 'metal-centred free radicals', $[M(CO)_nL_m]^{\bullet}$.[1b] Of particular interest have been the reactions of such radicals which are believed to involve oxidative addition processes. Thus, complexes such as $[Co(CO)_3(PBu^n_3)]_2$ react with $SnHBu^n_3$ to yield $[Co(SnBu^n_3)(CO)_3(PBu^n_3)]$ and H_2 by a complex mechanism in which the two critical steps are equations (2) and (3).[2] It has also been suggested that the photochemical reaction of $[Mn_2(CO)_8(PR_3)_2]$ (R = Bu, OEt) with HCl yielding $[Mn(H)(CO)_4PR_3]$ and $[MnCl(CO)_4PR_3]$, a reaction which is a *formal* oxidative addition across a metal–metal bond, involves oxidative addition of HCl to the intermediate, $[Mn(CO)_3PR_3]$, giving $[Mn(H)Cl(CO)_4PR_3]$, as the crucial step.[3]

$$[L_m(CO)_nM–M(CO)_nL_m] \rightleftharpoons 2[M(CO)_nL_m] \quad (1)$$

$$[M(CO)_nL_m] \rightleftharpoons [M(CO)_{n-1}L_m] + CO \quad (2)$$

$$M[M(CO)_{n-1}L_m] + SnHBu_3 \rightarrow [M(H)(SnBu_3)(CO)_{n-1}L_m] \quad (3)$$

$$[L_m(CO)_nM–M(CO)_nL_m] \rightleftharpoons [L_m(CO)_nM–M(CO)_{n-1}L_m] + CO \quad (4)$$

We have been interested in the reactions of dinuclear metal complexes with halogenoalkanes[4] and wished to examine such reactions under photochemical conditions, with the aim of employing the oxidative addition to produce halogeno and alkyl metal complexes. Since commencement of this work, others have reported that there is no evidence for CO dissociation from $[Mn(CO)_5]$, $[Mn(CO)_4PR_3]$, and $[Mn(CO)_3(PR_3)_2]$,[1a,5,6] and furthermore, there is now sound evidence that CO dissociation from metal carbonyl dimers [equation (4)] is a primary photoprocess which is able to compete effectively with metal–metal bond homolysis.[5,6] It is also noteworthy that in the case of $[Mn_2(CO)_{10}]$, the rate constant for the recombination reaction of equation (1) is approximately 10^3 times that of the recombination reaction of equation (4).[6]

We have now examined photochemical reactions between $Ph(CH_2)_nCl$ (n = 1,2) and $[Mn_2(CO)_8(PR_3)_2]$ (R = Et, Bu^n, OEt; 150 W mercury discharge lamp; hexane solution) and have observed the formation of equimolar amounts of $[MnCl(CO)_4PR_3]$ and $[Mn\{(CH_2)_nPh\}(CO)_4PR_3]$ as the only products† in reactions that proceed cleanly to completion in 2.5 h (R = Et) to 4.0 h (R = Bu^n). Similar reactions with $[Mn_2(CO)_8(PPh_3)_2]$ also yield products of this type, but are much slower, not having reached completion in 35 h. The reactions were monitored by following changes in i.r. spectra in the metal carbonyl region, the halogeno and alkyl metal complexes being produced at equal rates. When comparable reactions were performed under an atmosphere of CO, both products were again formed at identical, but reduced rates.

These findings contrast with the recently reported flash photogeneration of $[Mn(CO)_4PR_3]$ in the presence of halogeno- and polyhalogeno-alkenes which led to the observation of $[MnX(CO)_4PR_3]$ only.[7] However, we have found that observation of both halogeno and alkyl metal complexes is very dependent on the reaction system. Thus, while both products are observed in reactions involving $[Mn_2(CO)_8(PR_3)_2]$ and $Ph(CH_2)_nCl$ (n = 1, 2), reactions with $PhCH_2Br$ yield only $[MnBr(CO)_4PR_3]$. However, in separate experiments we have found that $[Mn(CH_2Ph)(CO)_4PBu^n_3]$ undergoes a rapid photochemical reaction with $PhCH_2Br$ leading to $[MnBr(CO)_4PBu^n_3]$, whereas no reaction is observed with $PhCH_2Cl$. We have also confirmed the findings of Brown and co-workers,[7] who observed that reactions of CCl_4 with $[Mn_2(CO)_8L_2]$ (L = CO, PBu^n_3) lead only to $[MnCl(CO)_4L]$, however, we have found both of these reactions to be inhibited by CO. Furthermore, we have observed that reactions between $[Mo_2(CO)_6(\eta\text{-cp})_2]$, $[Fe_2(CO)_4(\eta\text{-cp})_2]$, and $[Co_2(CO)_6(PBu^n_3)_2]$ and $PhCH_2X$ (X = Cl, Br) give only halogeno complexes together with dibenzyl (cp = cyclopentadienyl).

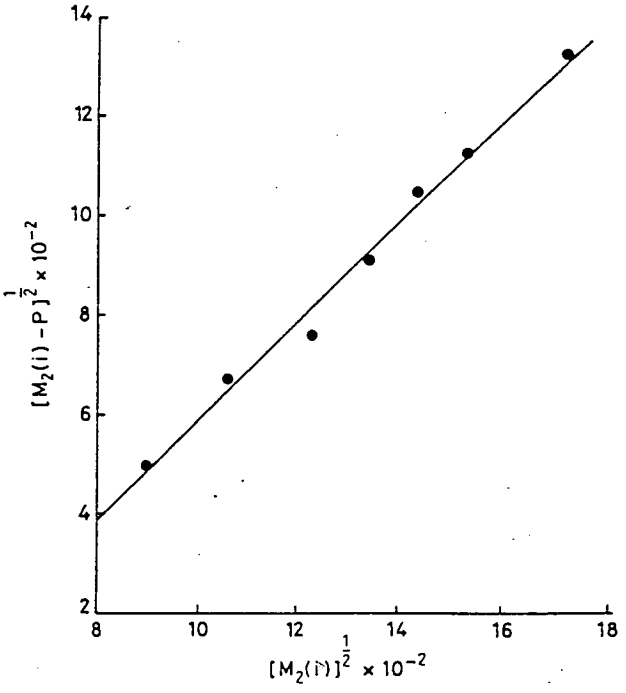

Figure 1. Plot of $[M_2(i)]^{\frac{1}{2}}$ *vs.* $[M_2(i) - P]^{\frac{1}{2}}$.

† Prolonged irradiation leads to the further production of small quantities of *mer*-$[MnCl(CO)_3(PR_3)_2]$.

$$[Mn_2(CO)_8(PR_3)_2] \overset{h\nu}{\underset{k_{-1}}{\rightleftharpoons}} 2[Mn(CO)_4(PR_3)]$$

$$[Mn(CO)_4PR_3] \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} [Mn(CO)_3PR_3] + CO$$

$$[Mn(CO)_3PR_3] + R'X \xrightarrow{k_3} [Mn(R')X(CO)_3PR_3]$$

$$[Mn(R')X(CO)_3PR_3] + [Mn(CO)_4PR_3] \xrightarrow{k_4} [MnR'(CO)_3PR_3] + [MnX(CO)_4PR_3]$$

$$[MnR'(CO)_3PR_3] + CO \xrightarrow{k_5} [MnR'(CO)_4PR_3]$$

Scheme 1

$$[Mn_2(CO)_8(PR_3)_2] \overset{h\nu}{\underset{k_{-1}}{\rightleftharpoons}} 2[Mn(CO)_4PR_3]$$

$$[Mn(CO)_4PR_3] + R'X \xrightarrow{k_2} [Mn(CO)_4PR_3]^+ + R'X^{\cdot -}$$

$$R'X^{\cdot -} \xrightarrow{k_3} R'^{\cdot} + X^-$$

$$[Mn(CO)_4PR_3]^+ + X^- \xrightarrow{k_4} [MnX(CO)_4PR_3]$$

$$[Mn(CO)_4PR_3] + R'^{\cdot} \xrightarrow{k_5} [MnR'(CO)_4PR_3]$$

Scheme 2

In order to probe the mechanism of these reactions in more detail, we have carried out a kinetic study of the reaction between $[Mn_2(CO)_8(PBu^n_3)_2]$ and $PhCH_2Cl$, employing a thermostated merry-go-round photoreactor.‡ Figure 1 shows the reaction rate to be proportional to $\{[Mn_2(CO)_8(PBu^n_3)_2]\}^{\frac{1}{2}}$,§ a finding that suggests metal–metal bond scission is an important feature of the reaction. It has not been possible to measure the reaction order with respect to $PhCH_2Cl$, as the balance between solubility limitations and measurable reaction rates makes it impossible to obtain pseudo-first order conditions $\{[Mn_2(CO)_8(PBu^n_3)_2] \geqslant 10[PhCH_2Cl]\}$.

Mechanisms consistent with the experimental findings are shown in Schemes 1—3. In view of the facts that $[Mn(CO)_4PR_3]$ has been found not to undergo CO dissociation[1a] but that all the reactions of $[Mn_2(CO)_8L_2]$ (L = CO, PR_3) with halogenoalkanes reported here are inhibited by CO, we do not favour the mechanism shown in Scheme 1. The mechanism shown in Scheme 2 does not require a CO dissociation step and thus should not strictly be subject to inhibition by added CO. However, the 16-electron intermediate, $[Mn(CO)_4PR_3]^+$ would probably be susceptible to capture by CO leading to the known stable cation, $[Mn(CO)_5PR_3]^+$, thereby inhibiting the reaction. If this were the case, it might be expected that i.r. absorptions arising from the 18-electron cation[8a] would be observed and that the rate of production of the halogeno complex would be retarded, while that of the alkyl complex is unaffected. Neither of these phenomena is observed.

$$[Mn_2(CO)_8(PR_3)_2] \overset{h\nu}{\underset{k_{-1}}{\rightleftharpoons}} [Mn_2(CO)_7(PR_3)_2] + CO$$

$$[Mn_2(CO)_7(PR_3)_2] \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} [Mn(CO)_3PR_3] + [Mn(CO)_4PR_3]$$

$$[Mn(CO)_3PR_3] + R'X \xrightarrow{k_3} [Mn(R')X(CO)_3PR_3]$$

$$[Mn(R')X(CO)_3PR_3] + [Mn(CO)_4PR_3] \xrightarrow{k_4} [MnR'(CO)_3PR_3] + [MnX(CO)_4PR_3]$$

$$[MnR'(CO)_3PR_3] + CO \xrightarrow{k_5} [MnR'(CO)_4PR_3]$$

Scheme 3

We, therefore, favour the mechanism shown in Scheme 3. This is in accord with the experimental findings and the relative recombination rates of equations (1) and (4). As yet, we have no direct evidence for the third step, the oxidative addition of R'X to $[Mn(CO)_3PR_3]$, but believe it is a reasonable postulate in view of the fact that such a species would almost certainly have three unpaired electrons, thereby displaying an electronic configuration analogous to $[V(\eta\text{-}cp)_2]$. Vanadocene has been shown to react with alkyl halides to produce $[VR(\eta\text{-}cp)_2]$ and $[VX(\eta\text{-}cp)_2]$ by a mechanism involving formation of $[V(R)X(\eta\text{-}cp)_2]$.[8b]

Thus, although the reaction discussed above could be viewed as a *formal* oxidation addition across a metal–metal single bond, the reaction proceeds by interaction between the alkyl halide and mononuclear intermediates.

We thank the S.E.R.C. and the British Petroleum Co. PLC for financial support and Dr. G. Morris (B. P. Research Centre) and Dr. J. Betts (Kingston Polytechnic) for helpful discussions.

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‡ The reaction rate was measured by monitoring the production of $[MnCl(CO)_4(PBu^n_3)]$ by means of i.r. spectroscopy. The results obtained in this way display greater accuracy since the enhanced stability of this compound, compared to the benzyl analogue, allows it isolation in a higher state of purity. This, together with its higher stability leads to more accurate measurement of molar absorptivities of the CO stretching frequencies. However, monitoring the rate of production of $[Mn(CH_2Ph)(CO)_4(PBu^n_3)]$ gives essentially the same results.

§ The merry-go-round reactor enables product concentrations to be measured in a series of solutions containing different concentrations of starting material, but all irradiated for the same period of time. The rate expression is thus integrated to give an expression relating initial reactant concentration to product concentration. In this case this leads to the expression $[M_2(i)]^{\frac{1}{2}} - kt = [M_2(i) - P]^{\frac{1}{2}}$ where $M_2(i)$ is the initial concentration of metal dimer and P is the concentration of product at time, t. It is this relationship which is plotted in Figure 1.

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A STUDY OF COMPLEXES FORMED BETWEEN METAL IONS AND SOME AGRICULTURAL CHEMICALS

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ABSTRACT

2-Dimethylamino -5,6-dimethylpyrimidin-4-ol (I) and 5-n-butyl -2-dimethylamino-6-methylpyrimidin-4-ol (dimethirimol) form 1:1 complexes with Cu(II), Cd(II), Mn(II), Co(II), and Hg(II) salts. The infrared spectra of the complexes indicate that these pyrimidine bases bond to the metal ions through the carbonyl group at C(4).

INTRODUCTION

Interaction between agricultural chemicals released into the environment and other chemical species therein is of interest from the point of view that the interaction could either inhibit or enhance the desired properties of the agrochemical. Pyrimidine bases play an important role in agricultural chemistry, and compounds such as 2-dimethylamino-5,6-dimethylpyrimidin-4-yl-dimethylcarbamate (pirimicarb) is used as an insecticide, whilst 5-n-butyl-2-dimethylamino-6-methylpyrimidin-4-ol (dimethirimol) is used as a systemic fungicide. Pirimicarb is readily hydrolysed under environmental conditions to 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (I) and thus (I) may be present in field situations whenever pirimicarb is used. Possible modes of environmental degradation of dimethirimol and of (I) have previously been investigated (ref.1). Reports that the nucleic acid pyrimidines, thymine and uracil (ref.2), and other structurally related pyrimidines (ref.3), form complexes with metal salts prompted us to investigate the interaction between (I) and dimethirimol and a series of metal salts, especially since such salts may also be present in the environment.

METHODS

Dimethirimol was a gift from Plant Protection Division, I.C.I.Ltd. Compound (I) was prepared by a previously described method (ref.4).

Complexes were prepared by the following method. Pyrimidine compound

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(1m mol) and metal salt (1m mol) were dissolved respectively in 25 cm^3 of dry ethyl acetate and 10 cm^3 of dry ethanol in a Schlenk tube. The solutions were degassed by a thrice repeated freeze-thaw cycle under high vacuum, and then the solution of pyrimidine compound was added via a transfer tube and under nitrogen into the solution of metal salt. In cases where a precipitate formed on mixing, the solution was stirred for two hours, the precipitate filtered off and washed with 15cm^3 of dry ethyl acetate under nitrogen. The product was dried in vacuo and then stored in a sealed tube under vacuo prior to elemental analysis. In cases where a precipitate was not formed on mixing the reactants, the solution was refluxed until a precipitate formed and the foregoing procedure then carried out.

Infrared spectra were recorded in KBr discs on a Unicam SP-200 spectrophometer.

RESULTS AND DISCUSSION

Analytical data for complexes formed between (I) and various metal salts are listed in Table 1. It is evident from the data that 1:1 complexes are formed between (I) and the metal salts. Likewise, analytical data for complexes formed between dimethirimol and the same metal salts show that 1:1 complexes are formed in these systems also.

TABLE 1

Analytical results (%) for complexes formed between (I) and some metal salts.

Complex	Colour	Found			Calculated		
		C	H	N	C	H	N
$CuCl_2$(I)	Green	32.90	4.55	14.02	31.85	4.34	13.93
$CdBr_2$(I)	White	21.16	2.93	9.08	21.87	2.98	9.56
$CdCl_2$(I) .H_2O	White	26.04	3.60	11.30	26.07	4.10	11.40
$MnCl_2$(I) 0.5H_2O	White	31.98	4.77	13.86	31.80	4.67	13.91
$HgCl_2$(I)	White	22.26	3.15	9.70	21.91	2.98	9.58
$CoCl_2$(I) .2H_2O	Blue	28.00	4.50	11.93	28.85	5.14	12.62

The mode of bonding of (I) and of dimethirimol to the metal ion in the complexes was investigated by comparing the infrared spectra of (I) and of dimethirimol with the infrared spectra of the individual complexes. The spectrum of (I) is shown in Fig.1a along with the spectrum of the complex formed with cobaltous chloride. The spectra of all the complexes are closely similar with regard to their main features and that of Fig.1b represents a typical spectrum.

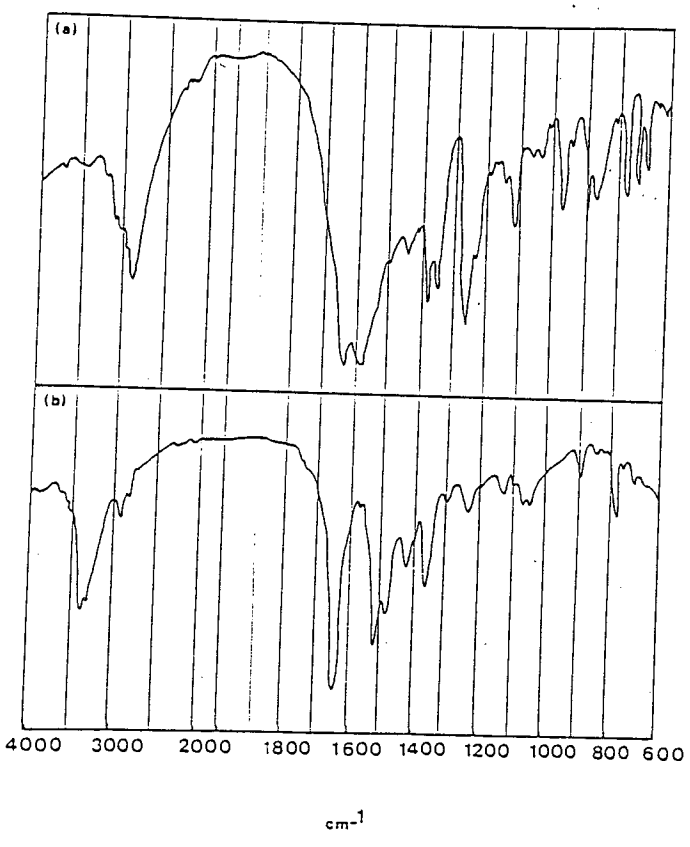

Fig.1. The infrared spectra of (a) compound (I), and (b) the complex formed with cobaltous chloride.

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Compound (I) exists in the keto form and its infrared spectrum closely resembles that of N-methylacetamide over the region 1200-1600 cm^{-1}. Based on the analysis made of the latter spectrum (ref.5), the bands in the spectrum of (I) at 1620, 1580 and 1250 cm^{-1} can be assigned to amide I, amide II and amide III vibrations respectively. These vibrations are of a complex form but have principal components involving in-plane N-H deformations coupled with C=O stretching. It can be seen from Fig.1 that significant changes occur with respect to these bands on complexation. This indicates that bonding of (I) to the metal ion could occur via the carbonyl oxygen which is acting as the donor atom. This is in accord with previous findings, based on infrared spectra, for the complexation of thymine and uracil to metal ions (ref.2). The strong bands around 1500 cm^{-1} which are present in the spectra of the complexes but not that of (I) could well arise from amide-type vibrations which have been modified in energy relative to those in (I) because of the bonding of (I) to the metal via the carbonyl oxygen. A further effect of this interaction could be to alter the energy of the N-H stretching vibration in the pyrimidine moiety. Comparison of Figs.1(a) and (b) shows that the broad band around 3000 cm^{-1} in the spectrum of (I) moves to 3350 cm^{-1} on complexation and no longer overlaps the C-H stretching bands at just below 3000 cm^{-1}.

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Chlorophyll Sensitised Photodegradation of 2-Dimethylamino-5,6-dimethylpyrimidin-4-ol

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ABSTRACT

The chlorophyll sensitised photodegradation of 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (**I**)*, a hydrolysis product of pirimicarb, in the solid state on silica gel and in chloroform solution has been investigated. The product distribution in the solid state photodegradation was different from that in chloroform solution and was dependent upon the wavelength range of the incident radiation. When radiation of wavelength greater than 420 nm was used, the products formed in the chlorophyll sensitised degradation of* **I** *in the solid state were similar to those obtained when Rose Bengal or Methylene Blue were used as sensitisers. These results indicate that singlet oxygen is implicated in the sensitised photodegradation of* **I** *in the solid state. Numerous products were formed in each of the systems studied.*

1 INTRODUCTION

The importance of pyrimidine bases in agricultural chemistry is illustrated by the use of ethirimol (5-butyl-2-ethylamino-6-methylpyrimidin-4-ol) and dimethirimol (5-butyl-2-dimethylamino-6-methylpyrimidin-4-ol) as systemic fungicides, and of pirimicarb (2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate) as an insecticide. The mode of degradation of agrochemicals under the influence of light and oxygen is of interest and previous investigations of the degradation of pyrimidine bases under such conditions indicate that singlet oxygen could have a role in the degradation process.[1,2] Singlet oxygen is readily formed via the uptake of visible radiation by a coloured sensitiser which subsequently transfers the absorbed energy to ground state molecular oxygen; singlet oxygen is a highly

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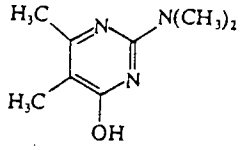
reactive electrophile.[3–6] Chlorophyll is known to act as a sensitiser for singlet oxygen production[7] and, since chlorophyll is a primary light absorber in the environment, the ability of chlorophyll to sensitise the photodegradation of pyrimidine bases has been investigated. The present paper reports on the chlorophyll sensitised photodegradation of 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (I), a compound which is released into the environment on the hydrolysis of pirimicarb (ICI plc. Plant Protection Division; private communication).



I

2 EXPERIMENTAL METHODS

[2-^{14}C]I was supplied by ICI plc, Plant Protection Division. Chlorophylls *a* and *b* were extracted from spinach leaves and purified as previously described.[8] Rose Bengal and Methylene Blue (Aldrich Chemical Co Inc) were used as supplied.

The photo-reactor used in experiments consisted of six 100-watt standard light bulbs mounted radially around a central sample well, the whole being housed in a light-tight container. The light from the bulbs was filtered through Kodak 'Wratten' gelatine filters which removed radiation of wavelength shorter than 420 nm. Samples for photolysis in solution were housed in a 40-cm^3 glass reaction vessel, thermostatted at 20°C, which was located at the centre of the well at a distance of 60 cm from the light sources. Typically, 5 cm^3 samples were removed at 15 min intervals during photolysis, evaporated almost to dryness under reduced pressure and applied to a t.l.c. plate prior to development.

The samples for photolysis in the solid state were made up in methanol solution and spotted onto Merck silica gel F_{254} plates (0·2 mm layer thickness × 20 cm × 20 cm). Compound I was applied first and the amount of material applied to a particular spot was controlled so that the ^{14}C-activity at each spot along the baseline was within 5% of the activity of the spot used as the reference blank. Solvent was evaporated after each application and also prior to the application of sensitiser to the spot regions. The t.l.c. plates were mounted in a holder and were covered with a Kodak 'Wratten' gelatine filter when they were to be exposed to radiation of wavelength greater than 420 nm. The plate holder was mounted at the centre of the photolytic reactor and the t.l.c. plate exposed to radiation from the six 100-watt light bulbs. When plates were to be exposed to sunlight they were placed in a thin, perforated polythene bag transparent to radiation of wavelength greater than 300 nm. After photolysis the t.l.c. plates were developed directly.

One-way chromatography was carried out using chloroform+methanol (95+5 by volume) as eluent, whilst two-way chromatography was carried out using acetone+water (98+2 by volume) as initial eluent and butan-1-ol+acetic acid+water (12+3+5 by volume) as second eluent. Two-way chromatograms

TABLE 1
Spray Reagents for the Detection of Guanidines and Ureas

Compound	*Spray reagent*	*Positive result*
Ureas	Cobalt (II) nitrate (1 g) and *p*-dimethylaminobenzaldehyde (1 g) dissolved in ethanol and sprayed. Plate exposed to HCl vapour when dry.	Intense yellow spots on an intense green background
Guanidine	Ethanolic Bromocresol green	Blue spot
N-methyl guanidine, and *N,N*-dimethyl guanidine	(a) 10 g litre^{-1} α-Naphthol in 2-M NaOH	Purple spots on a green background
	(b) 1 g litre^{-1} Diacetyl in H_2O	
	Equal quantities of (a) and (b) mixed, plate sprayed and then heated for 3 min at 100°C	

were obtained by extracting material from selected regions on a one-way chromatogram into methanol, concentrating to small volume, and then spotting onto one corner of a t.l.c. plate prior to development.

Autoradiograms were obtained by placing the developed plate in contact with X-ray film (Kodak NS 59T), covering with black polythene, and exposing the film for a period of time, typically 56 h. After exposure the film was developed and fixed using Ilford X-ray photographic chemicals. The entire operation was carried out in a dark room fitted with Kodak 6B safelights.

Urea, *N*-methylurea, *N,N*-dimethylurea, guanidine, *N*-methylguanidine and *N,N*-dimethylguanidine were used as standards for their identification in product mixes. These compounds were detected on two-way chromatograms using the spray reagents described in Table 1.

3 RESULTS

The autoradiogram depicted in Fig. 1 is from the chlorophyll sensitised photodegradation of **I** in chloroform solution. It can be seen from Fig. 1 that as the photolysis proceeds there is a decrease in the amount of **I** detected in the autoradiogram and a concomitant increase in the amount of product material appearing on the baseline of the autoradiogram. Two-way chromatography on this 'baseline' material revealed that a number of products were present and, of these, the spots labelled as **a**, **b**, and **c** in Fig. 2 were identified as *N,N*-dimethylurea, *N*-methylurea and *N,N*-dimethylguanidine respectively.

Figure 3 illustrates the autoradiogram arising from the sensitised photodegradation of **I** on silica gel using radiation of wavelength greater than 420 nm. The autoradiogram shows that there is no significant degradation of **I** in the absence of sensitiser and that the product distribution in the presence of sensitiser appears to be largely independent of the nature of the sensitiser. Two-way chromatography of the 'baseline' material seen in the autoradiogram from

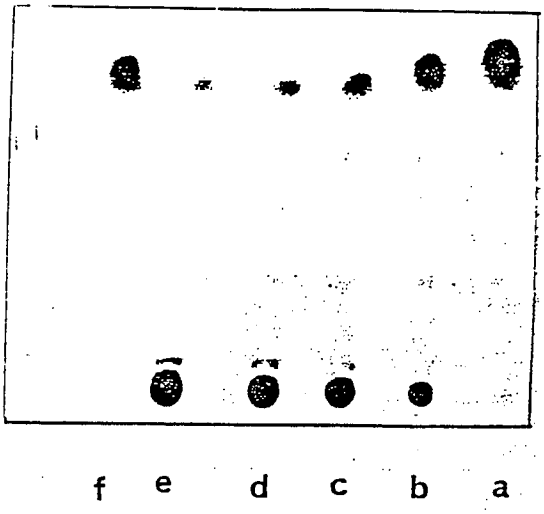


Fig. 1. Autoradiogram resulting from photolysis of a solution of [2-^{14}C]I ($7{\cdot}5\times10^{-4}$ M) and a mixture of chlorophylls *a* and *b* (approximately 6×10^{-5} M) in chloroform. Photolysis time (h): (a) 0, (b) 0·25, (c) 0·5, (d) 0·75, (e) 1·0. Wavelength of radiation >420 nm. Autoradiogram (f) is for I run as standard.

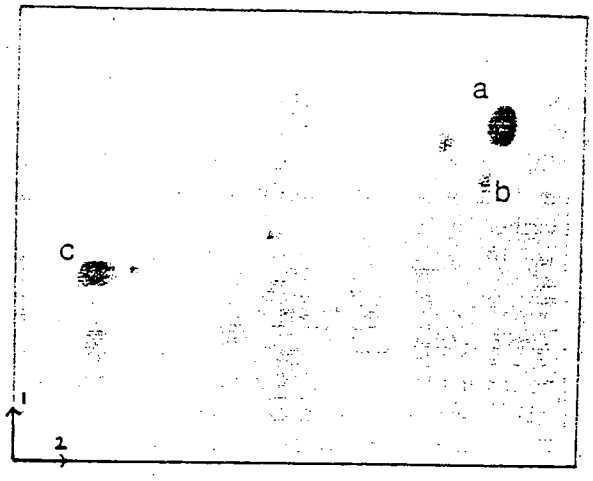


Fig. 2. Autoradiogram resulting from two-way chromatography of product material appearing on baseline of autoradiogram of Fig. 1. (a) *N,N*-dimethylurea, (b) *N*-methylurea, (c) *N,N*-dimethylguanidine.

the chlorophyll sensitised degradation (Fig. 3(b)) gave rise to the autoradiogram of Fig. 4.

When sunlight was used to initiate the photodegradation of I in the solid state the product distribution was as shown on the autoradiogram of Fig. 5. Figure 6 shows the autoradiogram resulting from two-way chromatography of the product mixture appearing on the baseline of the autoradiogram from the chlorophyll

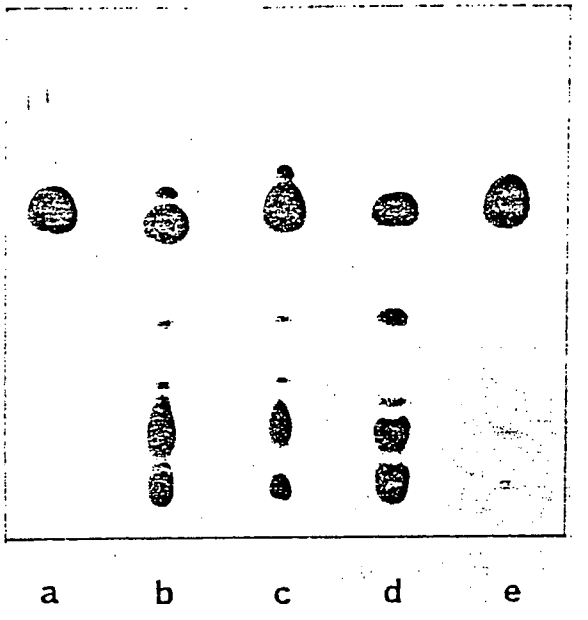


Fig. 3. Autoradiogram resulting from sensitised photodegradation of I in the solid state on silica gel. (a) I run as a standard after photolysis: Sensitiser: (b) chlorophylls *a* and *b*, (c) Methylene Blue, (d) Rose Bengal, (e) none. Wavelength of radiation >420 nm.

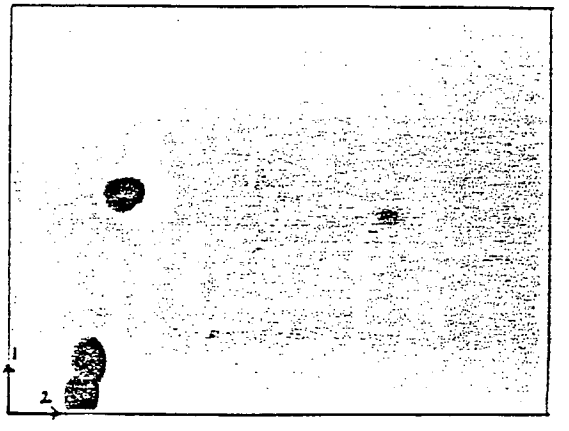


Fig. 4. Autoradiogram resulting from two-way chromatography of product material appearing on baseline of autoradiogram (b) of Fig. 3.

sensitised degradation of I (Fig. 5(a)). The autoradiogram of Fig. 6 is closely similar to those obtained from the product mixtures appearing on the baseline of the autoradiograms of Figs 5(b) and 5(c), but differs to some extent from that of Fig. 7 which was obtained by two-way chromatography of the 'baseline' products (Fig. 5(d)) formed in the direct photodegradation of I, i.e. in the absence of sensitiser.

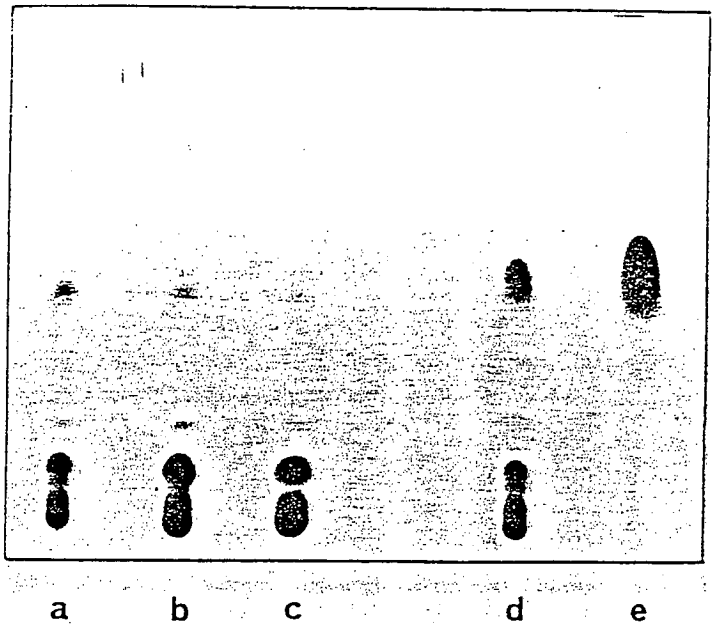


Fig. 5. Autoradiogram resulting from sunlight initiated photodegradation of I in the solid state on silica gel. Sensitiser: (a) chlorophylls *a* and *b*, (b) Methylene Blue, (c) Rose Bengal, (d) none, (e) none, I run as a standard after photolysis.

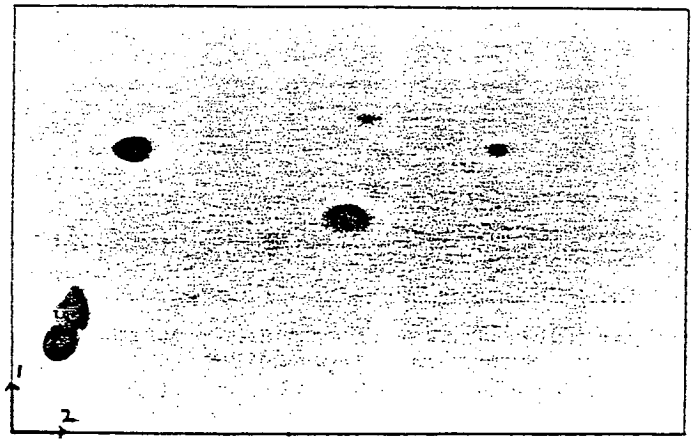


Fig. 6. Autoradiogram resulting from two-way chromatography of product material appearing on baseline of autoradiogram (a) of Fig. 5.

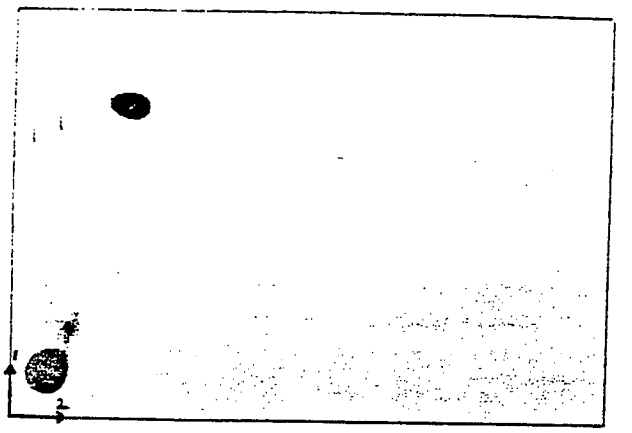


Fig. 7. Autoradiogram resulting from two-way chromatography of product material appearing on baseline of autoradiogram (d) of Fig. 5.

4 DISCUSSION

Rose Bengal and Methylene Blue are widely used as sensitisers for the formation of singlet oxygen,[3-6] and it has been shown previously[2] that the Rose Bengal sensitised photo-oxidation of I occurs via reaction with singlet oxygen. Chlorophyll also acts as a singlet oxygen sensitiser,[7] and the similarity found herein between the product distributions in the Rose Bengal, Methylene Blue and chlorophyll sensitised photodegradation of I suggests that singlet oxygen could well participate in this process.

It is of interest that the chlorophyll sensitised photodegradation of I in chloroform solution does not lead to any significant amount of 'non-baseline' products (Fig. 1) in contrast to the sensitised photodegradation in the solid state (Fig. 3). The difference in products between photodegradation in chloroform solution and in the solid state is also seen on comparing the autoradiograms (Figs 2 and 4). For example, the photodegradation of I in chloroform leads to the formation of *N,N*-dimethylurea and *N*-methylurea, neither of which are formed in the photodegradation in the solid state. Furthermore, the material remaining on, or close to, the origin in the two-way autoradiogram from the 'baseline' products of the solid state photolysis (Fig. 4) is not observed in the corresponding autoradiogram from the 'baseline' products of the solution photolysis (Fig. 2).

Previous studies have shown that singlet oxygen attacks I at the 5,6-double bond of the pyrimidine moiety. The mode of reaction of singlet oxygen at nitrogen activated double bonds of this type is well characterised,[3-6] and reaction either occurs via an *ene* process to give a hydroperoxide as initial product or via a 1,2-cycloaddition process to give a dioxetane as initial product (Fig. 8). With systems in which both reaction pathways can occur the polarity of the reaction medium controls the balance between the pathways,[9-12] with non-polar solvents giving rise preferentially to 'ene'-type products and polar solvents to 'dioxetane'-type pro-

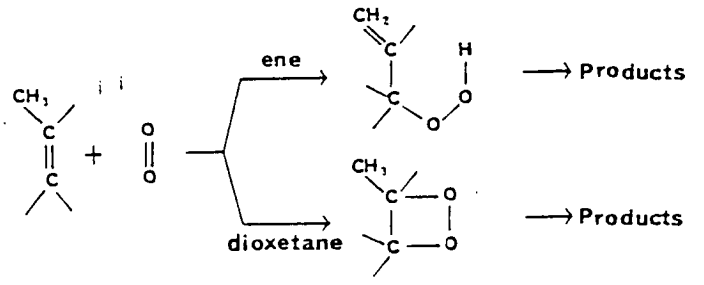


Fig. 8. Modes of reaction of singlet oxygen with ethene systems.

ducts. It is quite possible, therefore, that the difference between the products formed in chloroform solution and on silica gel arises because of the difference in polarities of the reaction media. In both cases the number of products ultimately formed is relatively large, with at least ten products being observed in the autoradiograms depicted in Figs 2 and 4. The number of products actually formed will be greater than that observed since only those products carrying the ^{14}C label will show up on an autoradiogram. The complexity of the product mixtures precluded characterisation of the products other than by use of t.l.c. standards as described.

The nature of the products formed in the sensitised degradation of I in the solid state is dependent upon the wavelength range of the incident radiation. Comparison of Figs 3 and 5 reveals that a greater variety of 'non-baseline' products are formed when radiation of wavelength greater than 420 nm is used, as compared to the situation where sunlight is used. The difference is further highlighted on comparing Figs 4 and 6 when it can be seen that the 'baseline' product mix in the chlorophyll sensitised degradation of I using sunlight differs from that when radiation of wavelength greater than 420 nm is used. The wavelength range of sunlight extends down to the region 300–320 nm and since I is known to undergo photochemical transformations when photolysed with radiation in this wavelength region,[13] it is to be expected that products from the direct photolysis of I and also from the sensitised degradation of I will be present in sensitised reactions when sunlight is the radiation source. The 'baseline' products from the direct (non-sensitised) photodegradation of I in the solid state using sunlight are shown in Fig. 7. This product mix differs from those of Figs 4 and 6.

It can be seen from Fig. 5 that the rate of photodegradation of I in sunlight is greater in the presence than in the absence of sensitiser. This is shown by the almost complete removal of I in the presence of sensitiser as compared with its only partial removal in the absence of the latter. This could arise because the presence of sensitiser increases the proportion of radiation absorbed and utilised in the photodegradation. Furthermore, previous work[1,2] has shown that singlet oxygen reacts rapidly with I and thus generation of singlet oxygen via the intermediacy of a sensitiser under the conditions described would be expected to lead to rapid removal of I.

5 CONCLUSIONS

The absorption of visible light or the sun's radiation by chlorophyll and other sensitisers in the presence of compound **I** leads to the degradation of this compound. Since the sensitisers used are known to produce singlet oxygen which reacts rapidly with **I**, it is likely that singlet oxygen is involved in the degradation process. It may be concluded that chlorophyll has the potential to sensitise the degradation of **I** in the environment when light and oxygen are present.

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Products from the Sensitised Photo-oxidation of 2-Dimethylamino-5,6-dimethylpyrimidin-4-ol

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ABSTRACT

The products from the methylene blue sensitised photo-oxidation of 2-dimethylamino-5,6-dimethylpyrimidin-4-ol (I) in deuterochloroform/deuteroacetone have been investigated. A zwitterion and a hydroperoxide are formed initially, with the zwitterion predominating. The zwitterion compound degrades or reacts in the solid state on silica gel to give further products.

1 INTRODUCTION

The application of pyrimidine bases as agrochemicals is exemplified by the use of dimethirimol (5-butyl-2-dimethylamino-6-methylpyrimidin-4-ol) and ethirimol (5-butyl-2-ethylamino-6-methylpyrimidin-4-ol) as fungicides for the respective control of mildew in cereals and cucurbits, and of pirimicarb (2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate) as an insecticide. Such compounds can be subjected to sunlight photolysis in the environment, and in previous studies[1–4] the photochemistry of dimethirimol and ethirimol, and of the structurally related compound, 2-dimethylamino-5,6-dimethylpyrimidin-4-ol(I) have been investigated. Compound I is released into the environment on the hydrolysis of pirimicarb (ICI plc, Plant Protection Division; private communication).

The combination of sunlight, oxygen and a suitable absorber of radiation can lead to the formation of singlet oxygen, an energetic form of oxygen which has the chemical properties of a highly-reactive electrophile. Singlet oxygen is formed by a process whereby the absorbing compound transfers energy to ground-state molecular oxygen to give an electronically excited species of oxygen ($^1\Delta_g$) which has significantly long lifetimes in the gas phase and in solution. This form of oxygen has been detected in natural surface waters and been shown to act as an oxidising agent

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in this environment.[5,6] Singlet oxygen has been implicated in the photo-oxidation of thiabendazole fungicides,[7] pyrimidine based fungicides,[8,9] thioether-containing pesticides[10,11] and pyrethroid insecticides.[12] The photo-oxidation of compound I may also occur via a mechanism involving singlet oxygen.[13] In view of the increasing realisation that singlet oxygen may have an important role in the photodegradation of agricultural chemicals, a further study of the photo-oxidation of compound I has been carried out in order to gain information on the initial stages of the reaction sequence leading to degradation products.

Photo-excitation of methylene blue in the presence of oxygen leads to the formation of singlet oxygen which can then react with any electron-rich species present in the system.[14,15] Compound I is such a species and solutions of methylene blue and I have been photolysed at low temperature in order to trap the initial products formed in the reaction of singlet oxygen with I. The results of this work are reported herein.

2 EXPERIMENTAL METHODS

Compound I was prepared by the method described previously.[2] [2-^{14}C]I was supplied by Plant Protection Division, ICI plc. methylene blue (Aldrich Chemical Co. Ltd) was used as supplied. Deuteroacetone-d_6 (BDH Ltd) and deuterochloroform-d_3 (BDH Ltd) were 99·5 and 99·8 atom % pure respectively. ^{1}H- and ^{13}C-NMR spectra were recorded on a Jeol JNM-GX 400 spectrometer using tetramethylsilane as internal reference.

Samples were prepared for photolysis by pipetting a solution (4 ml) of methylene blue (2×10^{-5} M) and of I ($7{\cdot}5 \times 10^{-2}$ M) in deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume) into an NMR sample tube (10 mm o.d.). The tube was immersed in a dry-ice acetone bath at 195 K in a Pyrex vessel and irradiated through a window in the vessel with radiation from a 600 W tungsten-halogen lamp whilst dry oxygen was bubbled through the solution. ^{1}H-NMR spectra of photolysed solutions were obtained by directly placing the NMR tube in the spectrometer sample compartment maintained at 213 K. Spectra could then be obtained subsequently at any desired temperature. Photolysis of the reactant solution for an extended period, typically 6 h, resulted in the precipitation of a white crystalline solid. This material was filtered off on a sintered-glass filter at ambient temperature before being dissolved in deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume) and the ^{1}H- and ^{13}C-NMR spectra of the solution recorded.

Samples for analysis by thin layer chromatography (TLC) were prepared by pipetting a solution (0·5 ml) of methylene blue (2×10^{-5} M) and of [2-^{14}C]I (10^{-3} M) in deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume) into an NMR sample tube (5 mm o.d.). The solution was photolysed as described previously for ~4 h. After photolysis the reactant solution was spotted directly onto a Merck silica gel F_{254} plate (0·2 mm layer thickness × 20 cm × 20 cm). The plates were developed using chloroform + methanol (1 + 1 by volume) as eluent.

Autoradiograms were obtained by placing the developed plate in contact with X-ray film (Kodak NS 59T), covering with black polyethylthene, and exposing the film

for a period of time, typically 56 h. After exposure, the film was developed and fixed using Ilford X-ray photographic chemicals. The entire operation was carried out in a darkroom fitted with Kodak 6B safelights.

3 RESULTS AND DISCUSSION

Photolysis of a solution of methylene blue (2×10^{-5} M) and I ($7{\cdot}5 \times 10^{-2}$ M) in deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume) at 195 K with radiation of wavelength greater than 420 nm resulted in the precipitation of a white crystalline solid which gave rise to the ^{1}H-NMR spectrum shown in Fig. 1 and the ^{13}C-NMR spectrum shown in Fig. 2. Examination of the ^{1}H-NMR spectrum of the reaction solution after various times of photolysis showed the presence of the same set of signals as in Fig. 1 with the addition of signals arising from methylene blue and unreacted I. It can be inferred from this observation that the spectrum shown in Fig. 1 is that of the only product(s) formed in the photolysis system.

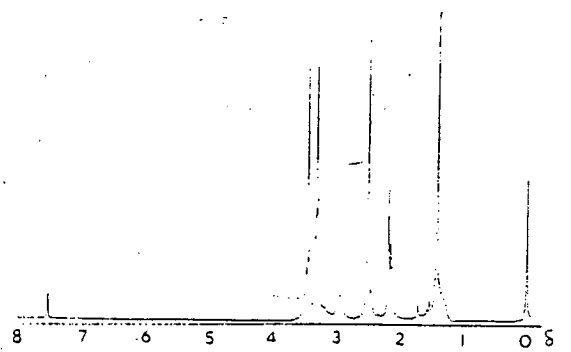


Fig. 1. ^{1}H-NMR spectrum of solid product from sensitised photo-oxidation of I. Solvent—deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume). Temperature—213 K. Resonances in the range 2·1–2·2δ and at 2·95δ are from the solvent.

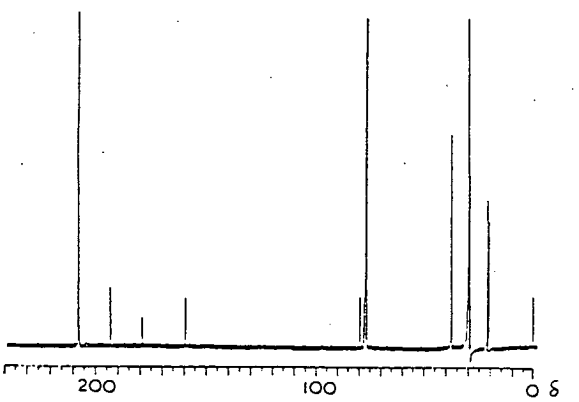
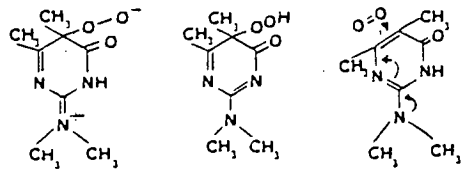


Fig. 2. ^{13}C-NMR spectrum of solid product from sensitised photo-oxidation of I. Solvent—deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume). Temperature—243 K.



A B C

Fig. 3. Structures of photolysis products.

Previous work[8] on the dye-sensitised photo-oxidation of I indicated that oxidation occurred at the 5,6-double bond of the pyrimidine moiety. The present results can be explained on this basis, and the ^{1}H-NMR spectrum, Fig. 1, can be interpreted in terms of the structures A and B (Fig. 3). The resonances at 1·42δ and 2·50δ can be assigned to the methyl protons at C-5 and C-6 respectively in both structures A and B, whilst the resonances at 3·31δ and 3·51δ can be assigned to the methyl protons in the dimethylamino group at C-2 in structure A. The methyl protons in the dimethylamino group in structure A are chemically non-equivalent because of restricted rotation about the C—N bond and give rise to two signals of equal intensity.

The resonance at 7·54δ in the spectrum, (Fig. 1) can be assigned to the proton of the hydroperoxide group in structure B. This assignment is in agreement with a previous report[16] of a proton resonance of this type at 7·06δ. The intensity of the signal for the proton in the hydroperoxide group is only about one-fifteenth of that of the individual signals for the methyl protons in forms A and B, indicating that the hydroperoxide form B is the minor component of the product mixture. Furthermore, on warming a solution which gave the resonances shown in Fig. 1 up to ambient temperature (293 K), the signal due to the proton of the hydroperoxide group in form B disappeared whilst the signals due to the zwitterion form A remained. In fact the signals due to the zwitterion were observable for some hours at a temperature of 323 K. The ^{13}C-NMR spectrum shown in Fig. 2 for the product isolated from the reaction of singlet oxygen with I is in accord with both the zwitterion structure A and the hydroperoxide structure B. As the zwitterion is the predominant component of the initial product mixture the assignments of the signals are made in Table 1 on the basis of the zwitterion.

The formation of the zwitterion can be explained by the electron shifts in structure C (Fig. 3), these shifts occurring on approach of singlet oxygen to the 5,6-double bond of I. The hydroperoxide would be formed by internal hydrogen atom transfer from the NH group. It is noteworthy that both zwitterion and hydroperoxide intermediates have been reported in the reaction of singlet oxygen with a variety of substrates,[16-18] and it has been proposed previously,[9] on the basis of thermodynamic data, that a zwitterion is formed in the reaction of singlet oxygen with I.

Photolysis of solutions of methylene blue (2×10^{-5} M) and [2-^{14}C]I(10^{-3} M) in deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume) at 195 K and at 293 K followed by spotting on a TLC plate and subsequent development gave the

TABLE 1
^{13}C-NMR Assignments for Zwitterion A

Chemical shift[a] δ	*Multiplicity*[b]	*Assignment*
20·69	quartet	$\underline{C}H_3$-C(5)
21·38	quartet	$\underline{C}H_3$-C(6)
37·39	2 × quartet	$(\underline{C}H_3)_2$-C(2)
75·56	singlet	$\underline{C}$(5)
159·31	singlet	$\underline{C}$(6)
179·04	singlet	$\underline{C}$(4)
193·28	singlet	$\underline{C}$(2)

[a] Proton decoupled spectrum. Internal reference—TMS. Solvent—deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume).
[b] Proton coupled spectrum. Internal reference—TMS. Solvent—deuterochloroform-d_3 + deuteroacetone-d_6 (1 + 1 by volume).

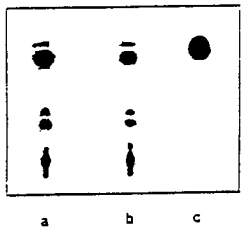


Fig. 4. Autoradiogram resulting from photolysis of a solution of methylene blue (2×10^{-5} M) and [2-^{14}C]I(10^{-3} M) in deuterochloroform-d_3/deuteroacetone-d_6 (1 + 1 by volume). Temperature of solution (a) 195 K, (b) 293 K. Autoradiogram (c) is for I run as a standard.

respective autoradiograms shown in Figs 4(a) and 4(b). A number of products are observable in both autoradiograms, but the number of products actually formed may be greater than that observed since only those products carrying the ^{14}C label will show up on an autoradiogram. Previous studies[13] would suggest that the products on the 'baseline' of the autoradiograms contain guanidines and ureas. It can be seen from Fig. 4 that the product distribution is the same for photolysis carried out at low temperature (195 K) and at ambient temperature (293 K). Thus the mechanism for the photo-oxidation of I is not affected by temperature. Since the zwitterion A is the only major species formed during photolysis, the products observed in autoradiograms 4(a) and 4(b) must be derived from this species. Furthermore, since it has been found that the zwitterion is stable in solution at ambient temperature the products must be formed as a consequence of reaction or breakdown of the zwitterion on contact with the silica gel of the TLC plate. This implies that if the zwitterion were to be formed in the environment on photo-oxidation of I and was in contact with plant or soil surfaces then it would react or break down to give further products.

4 CONCLUSIONS

The sensitised photooxidation of I in deuterochloroform-d_3/deuteroacetone-d_6 leads to the formation of a zwitterion as the major product. Although stable in

solution at ambient temperature and above, the zwitterion gives rise to various products when in the solid state and in contact with silica gel. The zwitterion would also be likely to break down or react to give products when in contact with plant or soil surface.

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An N.M.R. Study of Electron Donor–Electron Acceptor Interaction Between Aromatic Hydrocarbons and Diazines

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Abstract

Equilibrium constants have been measured by n.m.r. spectroscopy for the electron donor–electron acceptor interaction between a number of aromatic hydrocarbons and diazines. The values obtained have shown that the interaction is weak, and that the aromatic hydrocarbon acts as the electron donor and the diazine as the electron acceptor in the systems studied. Chemical-shift data have provided evidence for the relative positioning of the donor and acceptor components within the various complexes. The effect of temperature on the equilibrium constant for complex formation between ($^2H_6$)benzene and pyrazine has shown that the enthalpy of formation is close to zero.

Introduction

Interactions between nucleic acids and nucleotides and other species such as proteins, intercalating drugs and carcinogens are important aspects of recognition and binding in biological systems. The work which has been carried out indicates that different types of interaction are responsible for such binding, e.g., hydrogen bonding, stacking, electrostatic and hydrophobic interactions.[1,2] In the case of the aromatic amino acid tryptophan π–π stacking interactions occur with nucleic acid bases due to the strong π-electron-donating character of the indole ring system.[1–4]

Aromatic hydrocarbons are known to intercalate into DNA, a process which involves π–π interactions, and molecular associations between nucleic acids and aromatic hydrocarbons have been reported. (For a review of charge-transfer interactions of biomolecules see ref. 5.) Some workers have shown molecular associations between aromatic hydrocarbons and simple pyrimidines

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and purines,[6–8] but, although there has been much work carried out on more complex systems, there has been comparatively little published on relatively simple systems in which the effect of substitution patterns, positioning of the heteroatoms, etc., on the molecular interactions could be ascertained. It has been reported[9] that in complexes of purines and pyrimidines with aromatic hydrocarbons the heterocyclic compounds act as electron donors whilst other reports[6,7] show that heterocyclic compounds act as electron acceptors. A report of the contributions of the purine nitrogens to stacking association has been made;[10] this shows a dependence of the association constant upon the number of nitrogen atoms.

N.m.r. spectroscopy has proved a valuable technique for the study of molecular complexes formed between electron donor and electron acceptor species, especially as measurement of equilibrium constants for complex formation from concentration-dependent n.m.r. chemical-shift data has a number of important advantages over spectrophotometric methods.[11] Chemical shifts are generally insensitive to small concentrations of impurities, which may be formed by slow chemical reaction of donor with acceptor, whereas spectrophotometric methods cannot generally be used with confidence if there is a significant absorption by extraneous species at the wavelength of measurement. Ideally, with the spectrophotometric method, the absorbances of a series of solutions are measured at the wavelength(s) corresponding to the maximum absorption coefficient(s) for the intermolecular charge-transfer band(s), and for which the absorbance arising from free donor and acceptor (and solvent) is zero. In practice, there are very few systems where this set of conditions is even approached. In the usual n.m.r. determinations,[12] it is line positions not line intensities that are required. Because of the narrowness of n.m.r. lines there is less chance of the lines to be observed, usually of the acceptor, being masked by absorptions due to the donor or solvent compared to the corresponding situation in u.v.–visible spectroscopy. Furthermore, often more than one n.m.r. probe in an acceptor can be used, thus providing multiple sets of experimental data from which independent equilibrium parameters can be calculated. A further advantage of the n.m.r. method is that information can be gained on the structures of the complexes with regard to the relative positioning of the donor and acceptor components.

We have now undertaken a study by n.m.r. spectroscopy of complexes formed in solution between a number of diazines and aromatic hydrocarbons in order to ascertain their donor–acceptor relationship and to gain information on the structure of the complexes formed.

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Results and Discussion

When a donor, D, interacts with an acceptor, A, to give a 1:1 complex, DA, in equilibrium with its components, then the equilibrium constant, K, for complex formation is given by

$$K = [DA]/[D][A] \qquad (1)$$

In the n.m.r. experiment a single set of signals is observed for a given set of chemical-shift-equivalent nuclei in the A species, irrespective of whether the particular A molecules are complexed or not. For a system in which $[D]_0 \gg [A]_0$ [the subscript zero indicating the total (free plus complexed) concentration of the species], equation *(2)* becomes valid to a good approximation:[12]

$$\Delta/[D]_0 = -K\Delta + K\Delta_0 \qquad (2)$$

where Δ is the difference in shift between a signal in A in the absence of D and in the presence of an added amount of D equivalent to a concentration $[D]_0$, and Δ_0 is the difference between the chemical shift of a signal in A in the absence of D and when A is in the fully complexed form.

It has been argued[13] that it is incorrect to take Δ as the measure of the shift for the signal in the equilibrium mixture relative to that in solution where $[D]_0 = 0$. The argument is that Δ and Δ_0 are measured for a signal due to A alone in the pure solvent whereas they should be referred to A in a hypothetical solution containing the appropriate concentration $[D]_0$ but in which there is no specific complex formation. This suggestion derives from observations of line positions of single solutes in isotropic solvents (usually carbon tetrachloride) compared with those in anisotropic solvents (usually benzene). The shift difference 'aromatic solvent induced shift' has been ascribed to non-complexing collisions by molecules of the anisotropic solvent.[14] It has been suggested that this effect will operate in solutions containing D and A molecules and will be extra to 1:1 association. This effect is called 'additional unspecific shielding'.[14] For solutions under present conditions the effective anisotropic 'solvent' would be the mixture of D and the diluting solvent. In systems where additional unspecific shielding is operative plots according to equation *(2)* would be curved.[13]

In the systems studied herein plots of $\Delta/[D]_0$ against Δ according to equation *(2)* gave good straight lines, which indicated that in these systems only 1:1 complexes were formed and that termolecular complexes (D_2A) and additional unspecific shielding were not of significance. A typical plot is shown in Fig. 1.

Values of K and Δ_0 derived from plots of $\Delta/[D]_0$ against Δ are given in Table 1. In the case of complexes involving pyrimidine and pyridazine the values of K were derived from chemical-shift measurements on different proton sites in each compound, and for each compound the values of K so derived are the same within experimental error. This suggests again that the stoichiometry of the complexes is essentially 1:1. It was found that for

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pyrimidine the change in the chemical shift of the proton at the 2-position was too small to allow accurate measurement, and therefore values of K based on measurement of the signal from this proton are not given in Table 1.

It can be seen from Table 1 that the values for the equilibrium constants lie in the range 0·29–0·57 kg mol^{-1}. The low values for K show that only weak complexes are formed in these systems. The results in Table 1 also show that as the electron donor ability of the aromatic hydrocarbon increases, by virtue of an increase in the number of methyl group substituents in the benzene ring or by an increase in the number of aromatic ring systems, so the strength of complexation, as measured by the value of K, increases. This clearly reveals that the aromatic hydrocarbons are acting as the electron donors and the diazines as the electron acceptors in the complexes.

The highest values for K are those for the complexes of (^{2}H$_8$)naphthalene with pyrazine and pyrimidine. Since naphthalene has a more extended

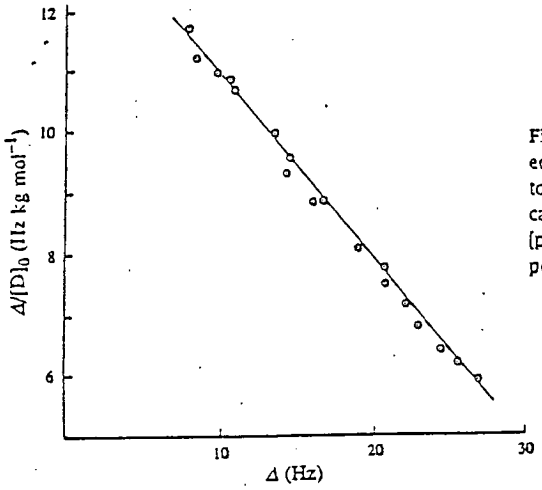


Fig. 1. Plot according to equation *(2)* for the toluene–pyrimidine system in carbon tetrachloride at 308 K: [pyrimidine] = 5·0×10^{-2} mol per kg of solution.

Table 1. Equilibrium constants (K, kg mol^{-1}) and chemical-shift values (Δ_0, Hz) for complexes of aromatic hydrocarbons with diazines in carbon tetrachloride at 308 K

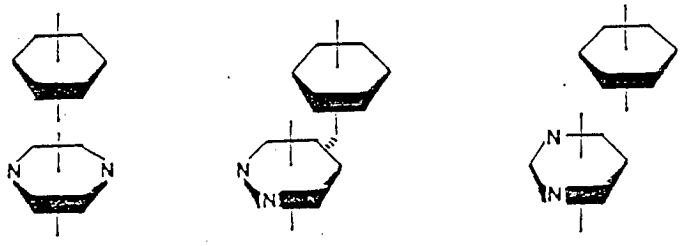
Estimated error in quoted values for K is ±0·01

Hydrocarbon	K	Δ_0	K	Δ_0	K	Δ_0	K	Δ_0	K	Δ_0
	Pyrazine		Pyrimidine				Pyridazine			
			H 4,6[A]		H 5[A]		H 3,6[A]		H 4,5[A]	
(^{2}H$_6$)Benzene	0·30	39	0·29	44	0·27	81	0·20	47	0·23	88
(^{2}H$_8$)Toluene	0·32	37	0·31	45	0·30	88	0·23	48	0·24	88
(^{2}H$_{10}$)-*o*-Xylene	0·34	43	0·35	44	0·33	84	0·30	44	0·30	80
(^{2}H$_{10}$)-*p*-Xylene	0·35	30	0·33	45	0·35	83	0·30	41	0·31	76
(^{2}H$_8$)Naphthalene	0·57	37	0·51	58	0·53	89	0·34	30	0·36	61
			5-Methylpyrimidine				4,6-Dichloropyrimidine			
			H 4,6[A]		CH_3[A]		H 2[A]		H 5[A]	
(^{2}H$_6$)Benzene			0·28	39	0·28	68	0·25	49	0·27	90

[A] Values of K and Δ_0 derived from measurement of chemical shift of numbered protons.

π-orbital system than the benzenoid hydrocarbons it will have a greater orbital overlap with the diazines, and this is manifested in a stronger charge-transfer interaction. It is of interest that for the complexes with ($^2H_8$)naphthalene the values of K lie in the order pyrazine > pyrimidine > pyridazine. The nitrogen atoms in pyrazine are in the *para* positions and the consequent symmetric electron density distribution means that the whole of the molecule will be involved in interaction with an electron donor. The electron density distribution in pyridazine is unsymmetrical in the sense that there is relatively high electron density at the 1- and 2-positions, where the nitrogen atoms are located, and relatively low electron density over the remainder of the molecule. Thus only part of the molecule will act as a charge acceptor and the lower extent of overlap with a donor as compared to pyrazine is manifested in a lower value of K.

The most likely position of the components within the 1:1 complex formed between the symmetrical donor benzene and the symmetrical acceptor pyrazine is as shown in structure (1).



(1) (2) (3)

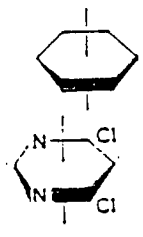
For complexes involving an acceptor with more than one type of proton, evidence for the time-averaged positions of the donor and acceptor can be gained from the values of Δ_0 for the different proton types.[15] If, for example, there are two proton types then the protons with the larger value of Δ_0 will be closer to the centre of the complex. It can be seen from Table 1 that for each aromatic hydrocarbon–pyridazine complex the value of Δ_0 for the protons at the 4,5-positions in pyridazine is approximately double that for the protons at the 3,6-positions. This indicates that for these complexes the aromatic hydrocarbon is preferentially sited over the 4,5-positions. A possible orientation for the components within the ($^2H_6$)benzene–pyridazine complex is shown in structure (2).

It is noteworthy that in the benzenoid hydrocarbon–pyrimidine complexes the Δ_0 values for the protons at the 4,6-positions in pyrimidine are similar to those for the protons at the 3,6-positions in pyridazine in the benzenoid hydrocarbon–pyridazine complexes. This would suggest that in these two sets of complexes H4,6 in pyrimidine and the H3,6 in pyridazine are approximately equidistant from the centre of the complex. A possible time-averaged structure for the ($^2H_6$)benzene–pyrimidine complex is shown in structure (3). In this

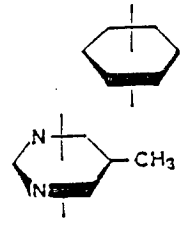
[15] Foreman, M. I., and Foster, R., *J. Chem. Soc. B*, 1969, 885.

structure the benzene donor is relatively far removed from the proton at the 2-position in pyrimidine, in accord with the observation that the change in chemical shift of this proton on complexation was too small to allow values of K and Δ_0 to be derived from the shift data.

Values for K and Δ_0 for complexes of ($^2H_6$)benzene with pyrimidine, 5-methylpyrimidine, and 4,6-dichloropyrimidine are given in Table 1. Although there are no marked differences in the equilibrium constants for formation of these complexes, there is a significant difference in the values of Δ_0 for protons at different positions in the acceptor moiety. Whereas the value of Δ_0 for the proton at the 2-position in pyrimidine and in 5-methylpyrimidine was found to be very small, the corresponding value in 4,6-dichloropyrimidine is relatively large, namely, 49 Hz. This clearly indicates that in the ($^2H_6$)benzene–4,6-dichloropyrimidine complex the benzene donor component is located on average more central to the pyrimidine ring system than in the complexes with pyrimidine and 5-methylpyrimidine. This presumably arises because of the charge deficiency created in the ring by the electron-withdrawing chloro substituents. A possible time-averaged orientation of the components of the ($^2H_6$)benzene–4,6-dichloropyrimidine complex is shown in structure (4). In this structure the benzene donor is closer to the 5-position than the 2-position, and this is reflected in the Δ_0 value of 90 Hz for the proton at the 5-position, as compared to 49 Hz for the proton at the 2-position.



(4)



(5)

The results given in Table 1 show that for the complex of ($^2H_6$)benzene with 5-methylpyrimidine Δ_0 value for the methyl protons is larger than that for the protons at the 4,6-positions. This, taken in conjunction with the observation that the Δ_0 value for the proton at the 2-position is very small, suggests that the benzene component is sited preferentially in the region over C5 and the methyl substituent. This is illustrated in structure (5).

The values of K and Δ_0 for the ($^2H_6$)benzene–pyrazine complex at different temperatures in carbon tetrachloride are as follows:

Temperature (K)	263	273	293	308	323	336
K (kg mol^{-1})	0·33	0·30	0·32	0·30	0·28	0·30
Δ_0 (Hz)	53	43	42	39	35	31

There is no significant change in the value of K (estimated error in quoted values is ±0·01) with temperature over the range 263–363 K; this indicates that the enthalpy of formation of the complex is zero or very close to zero. However, the results listed above show that there is a significant decrease in

the value of Δ_0 as the temperature increases. Thus the average separation between donor and acceptor species increases, and, as is to be expected, the complex becomes less tightly bound as the thermal energy of the system increases.

Experimental

AnalaR grade carbon tetrachloride was used as solvent. Pyrazine, pyrimidine and pyridazine were supplied by the Aldrich Chemical Company as 99+% pure, and were used without further purification. ($^2H_6$)Benzene, ($^2H_8$)toluene, ($^2H_{10}$)-*o*-xylene and ($^2H_{10}$)-*p*-xylene were supplied by the Aldrich Chemical Company as 99+ atom % ^2H, and ($^2H_8$)naphthalene was supplied as 98+ atom % ^2H. Solutions were made up with the concentration of diazine within the range 0·05–0·1 mol per kg of solution, and the concentration of aromatic hydrocarbon within the range 0·5–10·0 mol per kg of solution. The concentrations in any solution were always such that the concentration of aromatic hydrocarbon was always at least 10-fold that of the diazine. Chemical-shift measurements were made by using a Perkin–Elmer R32 sapectrometer operating at 90 MHz, with tetramethylsilane as internal reference. Each measurement was made in triplicate, and the results were averaged.

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